

# **EXHIBIT A**



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**Shah et al.**

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(54) **MULTILAYER NON-STICK COATING**

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**B32B 15/08; B32B 27/08; B32B 27/20**

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**427/407.1**

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**428/325, 328, 329, 330, 331, 411.1, 421,**  
**422, 457, 473.5, 474.4**

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(57) **ABSTRACT**

A non-stick coating formed on a substrate comprising a primer composition and a topcoat composition, wherein the primer composition is between the topcoat composition and substrate. The primer composition comprises at least one heat resistant adhesion promoter. The topcoat composition comprises at least one fluorocarbon resin and at least one heat resistant adhesion promoter other than a fluoropolymer that may be the same or different than the adhesion promoter of the primer composition. There are inorganic inert particles with an average particle size of at least about 10 micrometers contained in the primer composition. The invention includes the method for forming the coating.

**22 Claims, No Drawings**

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**MULTILAYER NON-STICK COATING****CROSS REFERENCE TO RELATED APPLICATION**

This application claims priority from Provisional application No. 60/410,712, filed Sep. 13, 2002.

**BACKGROUND OF THE INVENTION****1. Field of the Invention**

The present invention relates to a substrate coated with a non-stick coating.

**2. Prior Art**

Non-stick coatings are well known in the art. In these coatings normally fluorocarbon resins are used, since these resins have a low surface energy as well as thermal and chemical resistance. However, non-stick coatings solely based upon fluorocarbon resins suffer from poor adhesion to the substrate and poor scratch and abrasion resistance. Such coatings are easily damaged when cut with a knife or another metal tool. Rubbing or sanding also easily wears these coatings away.

It is known in the art that the adhesion can be improved by roughening of the (metal) substrate, e.g. by grinding, sand blasting, acid etching, brushing or baking a rough layer of glass, ceramic or enamel frit onto the substrate. This is disadvantageous since it is an additional step in the manufacturing process, which can be time consuming and/or requires the heating of the substrate.

To improve the adhesion to substrates and the mechanical properties (in particular, scratch resistance and abrasion resistance) of these coatings, the fluorocarbon resin is mixed with one or more heat resistant binder resins for better adhesion and one or more pigments and/or fillers for coloring and improvement of the mechanical properties.

Non-stick coatings may be applied in a single layer or as a multilayer coating.

U.S. Pat. No. 6,291,054 describes a multilayer non-stick coating wherein the undercoat (primer) comprises a mixture of a fluorocarbon polymer, a heat resistant binder, and large hard ceramic particles. The topcoat comprises a fluorocarbon resin. In the undercoat the heat resistant binder should improve the adhesion to the substrate, the fluorocarbon resin should improve the adhesion between the primer and the topcoat, and the large hard ceramic particles should improve the mechanical properties. However, the presence of the fluorocarbon resin (which has non-stick properties) lowers the adhesion of the primer to the substrate and the adhesion of the ceramic particles within the primer layer.

In WO 02/14066 a single layer non-stick coating is disclosed. This single layer comprises a binder resin, a fluorocarbon resin and filler material. However, this single layer non-stick coating has the same disadvantages as the three-component primer layer described above.

Surprisingly it was found that in a multilayer non-stick coating good adhesion between the primer layer and a next coating layer that is applied on top of the primer layer comprising a fluorocarbon resin can be obtained if the primer layer comprises a heat resistant binder and is substantially free of fluorocarbon resin. Therefore, the primer layer shows optimum adhesion to the substrate and to optionally present particles to improve the abrasion resistance of the coating, whereby the adhesion to the next coating layer is not compromised.

**SUMMARY OF THE INVENTION**

Accordingly, in one embodiment the present invention comprises a non-stick coating formed on a substrate com-

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prising a primer composition and a topcoat composition. The primer composition is between the topcoat composition and the substrate. The primer composition comprises at least one heat resistant adhesion promoter. The topcoat composition comprises at least one fluorocarbon resin and at least one heat resistant adhesion promoter other than a fluoropolymer that may be the same or different than the adhesion promoter of the primer composition. There are inorganic inert particles with an average particle size of at least about 10 micrometers contained in the primer composition.

In another embodiment, the invention comprises a method of applying a coating to a substrate comprising the sequential steps of:

- a. Preparing the surface of the substrate for said coating;
- b. Applying a primer composition comprising at least one heat resistant adhesion promoter and inorganic inert particles with an average particle size of at least about 20 micrometers;
- c. Applying a topcoat composition comprising at least one fluorocarbon resin and at least one heat resistant adhesion promoter other than a fluoropolymer that may be the same or different than the adhesion promoter of the primer composition; and
- d. Baking the coated substrate at a temperature from about 380° C. to about 440° C.

Other embodiments of the invention comprise details concerning compositions, relative amounts of ingredients, particle sizes and method steps.

**DETAILED DESCRIPTION OF THE INVENTION**

According to the present invention, the substrate, such as aluminum or aluminum shaped articles, is coated with a non-stick coating, wherein the coating is obtained by applying a primer composition and a topcoat composition, wherein the primer composition comprises a heat resistant resin as an adhesion promoter. It is preferred that the primer composition be substantially free of any fluorocarbon resin. The topcoat composition comprises at least one fluorocarbon resin. The topcoat also contains a heat resistant resin in addition to the fluoropolymer resin and is preferably the same heat resistant resin found in the primer composition.

**Primer Composition**

In addition to the heat resistant binder (adhesion promoter), the primer composition can comprise one or more of the following components: fillers, pigments, surfactants, solvents, defoamers, and any other component for a coating composition known to the person skilled in the art. More particularly, in a preferred embodiment, the primer composition comprises from about 10 wt. % to about 60 wt. % of the adhesion promoter, from about 10 wt. % to about 60 wt. % of the inorganic inert particles and from about 10 wt. % to about 60 wt. % of other ingredients selected from the group consisting of fillers, pigments, surfactants, solvents, defoamers and mixtures thereof, the wt. % being calculated on basis of the solid content of the primer composition.

The fillers in the primer composition may be selected from the group consisting of barium sulfate, calcium sulfate, calcium carbonate, silicas and silicates.

The primer composition may be substantially free of fluorocarbon resin.

**Topcoat Composition**

In addition to the fluorocarbon resin and heat resistant resin, the topcoat composition can comprise one or more of the following components: fillers, pigments, surfactants, solvents, defoamers, and any other component for a coating

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composition known to the person skilled in the art. Further the topcoat composition can comprise an acrylic resin and a catalyst. Components that can be present in the topcoat composition include butyl carbitol, triethanolamine, oleic acid, a hydrocarbon fluid, and a cerium based catalyst.

In a preferred embodiment the topcoat composition is a waterborne composition, wherein all ingredients are dispersed in water or are water-soluble.

In a preferred embodiment the topcoat composition also comprises at least 5 wt. % of a fluorocarbon resin dispersion wherein said resin is melt flowable at a temperature above 300° C. The presence of such resin will enable the manufacture of a non-stick coating with a smooth surface and good release properties.

In a preferred embodiment the topcoat composition comprises 55–70 wt. % of fluorocarbon resin dispersion, 3–10 wt. % of a fluorocarbon resin that is flowable at a temperature above 300° C., and 5–15 wt. % of an acrylic resin the wt. % being calculated on the basis of the solid content of the topcoat composition.

In another preferred embodiment, the topcoat composition comprises from about 1 wt. % to about 20 wt. % adhesion promoter, the wt. % being calculated on basis of the solid content of said topcoat composition.

#### Overcoat (Additional Layers)

If present, the over-coat layer, or layers, composition can comprise one or more of the following components: fillers, pigments surfactants, solvents, defoamers, and any other component for a coating composition known to the person skilled in the art.

In a preferred embodiment, the coating is obtained by applying an over-coat composition, such as a fluoropolymer rich clear-coat which is essentially free of pigments or fillers, after the topcoat composition is applied.

In a further preferred embodiment the over-coat layer composition comprises about 55–70 wt. % of a fluorocarbon resin dispersion, about 3–10 wt. % of a fluorocarbon resin that is melt flowable at a temperature above about 300° C., and about 5–15 wt. % of a film forming resin.

The preferred overcoat composition comprises at least one fluorocarbon resin, most preferably one that is flowable at a temperature above about 300° C.

#### Fluorocarbon Resin

Examples of fluorocarbon resins that can be used in the present invention include one or a mixture of fluorocarbons selected from the group consisting of polytetrafluoroethylene (PTFE), tetrafluoroethylene (TFE), hexafluoropropylene (HFP), perfluoropropylvinyl ether (PPVE), perfluoroalkyl vinyl ether, perfluoroalkyl vinyl ethylene co-polymers. Commercial examples are copolymers tetrafluoroethylene-hexafluoropropylene (FEP), tetrafluoroethylene-perfluoroalkyl vinyl ether copolymers (PFA) and ethylene-tetrafluoroethylene copolymers (ETFE).

If the contemplated application or use of the coated item is high temperature, the selection of fluoropolymer(s) should be those that are heat stable.

PTFE is an example of a heat resistant or stable fluorocarbon resins that can be used according to the present invention.

Fluorocarbon resins that are melt flowable at a temperature above 300° C. include copolymers of TFE, e.g., FEP and PFA.

The fluorocarbon resins are generally available as a dispersion of the polymer in water. In this dispersion the polymer particles have a small size (usually around 0.2 micrometers) and a surfactant is used to obtain a stable dispersion. For some polymers it is desirable to include an organic liquid in the dispersion.

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The fluorocarbon resin can also be present as a polymer powder, in which case normally an organic liquid is used to mix the particles into the coating composition.

#### Heat Resistant Binder (Adhesion Promoter)

The heat resistant binder that is present in the primer composition is a polymer that is film-forming upon heating (such as by radiation), evaporation of the solvent, and is also thermally stable. The binder shows good adhesion to the substrate and to the fluoropolymer composition that is applied over the primer composition. Preferred binders are those that are soluble or solubilized in water or a mixture of water and one or more organic solvents for the binder. This solvent should be miscible with water. The solubility of the binder enhances the mixing of the binder with the other components that are present in the primer composition.

An example of a suitable heat resistant binder component is a polyamic acid resin (PAI), which converts to a polyamideimide upon heating. This binder when fully imidized is able to withstand a continuous service temperature in excess of 250° C. In general, the polyamic acid is dissolved in a suitable combination of a solvent, such as N-methylpyrrolidone, water, and suitable tertiary alkyl amine. Another example of a suitable heat resistant binder component is polyethersulfone (PES). These polymers can withstand a continuous service temperature in the range from 170° C. to 190° C. Also polyphenylene sulfide (PPS) can be used as a heat resistant binder, either alone or in a mixture with PAI or PES.

Examples of heat resistant binders that can be used according to the present invention include Torlon® AI-10 (ex. Solvay), and Radel A-300 (ex. Solvay).

Preferred heat resistant adhesion promoters are selected from the group consisting of polyamideimide resins, polyethersulfone resins and polyphenylene sulfide resins, or combinations thereof.

A most preferred heat resistant adhesion promoter comprises polyamideimide resin.

#### Inorganic Inert Particles

The primer composition comprises inorganic particles with an average particle size of from about 10 micrometers to about 80 micrometers which are inert with respect to the other components that are present in the composition and can withstand a continuous service temperature in excess of 250° C. In addition, these particles are also stable at the eventual baking temperature of the non-stick coating. The particles are also not soluble in water or any other solvent that is present in the primer composition.

Examples of suitable inorganic particles include inorganic oxides, carbides or nitrides of elements in groups IIA–VB of the periodic table and natural minerals and mixtures thereof. Preferred inorganic particles include particles with an average particle size of at least 20 micrometers and more preferably in the range from about 20 to about 80 micrometers. The inorganic particles have a preferred Mohs hardness of at least about 5, more preferably a Mohs hardness of at least about 6. Examples of inorganic particles with Mohs hardness above 5 include alumina, zirconia, silicon carbide, titanium carbide, aluminum boride, and cristobalite.

In addition to the inorganic inert particles mentioned above, the coating compositions used according to the present invention can also comprise fillers, additives, and pigments that are commonly used in the preparation of coating compositions. Fillers can be any fillers known to those skilled in the art, e.g., barium sulfate, calcium sulfate, calcium carbonate, silicas or silicates (such as talc, feldspar, and china clay). Additives such as stabilizers, antioxidants, leveling agents, ant settling agents, matting agents, rheology

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modifiers, surface-active agents, UV light absorbers, light stabilizers, amine synergists, waxes, or adhesion promoters can also be added.

#### Application of the Coating

The substrates coated according to the present invention can be aluminum shaped articles, such as pots, pans, lids, mixing spoons, and all other utensils usually employed for food preparation and cooking (baking pans, oven racks etc.) as well as aluminum sheet to be shaped into the aforesaid articles. In both cases, the aluminum support is simply degreased according to any known method, e.g., in an alkaline or acid environment, or with organic solvents. In this treatment, the aluminum support maintains the surface roughness of the aluminum sheet, i.e. below 1.2 micrometers. In addition to the degreasing it is possible to roughen the surface.

The fluorocarbon resin may be applied as a dispersion of the resin in water with a surfactant.

Alternatively, the fluorocarbon resin may be applied as a polymer powder with an organic liquid.

#### EXAMPLES

The following applies to the examples given below:  
Scotch Brite Abrasion Test

The Scotch Brite Abrasion Test measures a coating's resistance to a constant scrubbing with an abrasive scouring pad. The vertical load on the scouring pad is set to 10 pounds (4.54 kg), and the scouring pad is changed every 10,000 strokes. The number of cycles that are required to scrape the coating down to bare metal is recorded in order to gauge the abrasion resistance of the non-stick system.

#### Scotch Brite Egg Release Test

The Scotch-Brite Egg Release Test is run in conjunction with the Scotch-Brite Abrasion Test. Every 10,000 strokes an egg is fried on the "wear track" created by the scouring pad to measure the extended food release properties of the non-stick system. Many non-stick coatings show very good release when the cookware is new, but over a few years of moderate use the release properties diminish very rapidly.

The number of cycles that a coating can endure before the egg sticks to the wear track is recorded to determine the true quality of a given non-stick system.

#### Hand Held Tiger Paw Test

The hand held "Tiger Paw" device is an industry-accepted standard, which was designed to test the resistance of a non-stick coating to long-term kitchen abuse. The Hand Held Tiger Paw consists of a weighted apparatus, which uses 3 "ball point" pens to scratch the coating film. The cookware which is being tested is filled with a thin layer of cooking oil, and heated to 400° Fahrenheit (205° Celsius).

The Tiger Paw is rotated over the non-stick surface in a circular fashion 2000 times, changing direction every 100 rotations. The coating is then examined for any fraying, blistering, or penetration to bare metal.

The invention will be elucidated with reference to the following examples. These are intended to illustrate the invention but are not to be construed as limiting in any manner the scope thereof.

#### Control 1

A primer comprised of 6.80 wt % polyamide-imide (Torlon@ AI 10 from Solvay) and 9.28 wt % PTFE (polytetrafluoroethylene dispersion, Fluon@ GP-1 from Asahi Glass) and a topcoat comprised of 59.54 wt % PTFE Dispersion (Polyflon@ 0-46) and 10.41 wt % Dyneon™ PFA 6900N Dispersion was applied to a non-gritblast hard anodized aluminum substrate in the form of a frying pan such that dry film thickness of 0.5 mil primer and 0.5 mil

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topcoat was obtained following a final bake of 427 deg C. (metal temperature) for 3-5 minutes. The resulting baked film was comprised of 24.2 wt % PAI and 19.8 wt % PTFE in the primer and 77.9 wt % PTFE and 4.56 wt % PFA in the topcoat layer.

#### Example 1

In an embodiment of the invention, A primer comprised of 33.0 wt % polyamideimide (Torlon@ AI 10 from Solvay), 38.0 wt % Silicon Carbide (#600-W from ELECTRO ABRASIVE POWDERS, average ps=11 microns) and no fluoropolymer component, and a topcoat comprised of 58.14 wt % PTFE Dispersion (Fluon@ GP1 from Asahi Glass) and 0.5 wt % polyamide-imide (Torlon@ AI 10 from Solvay) was applied to a non-gritblast hard anodized aluminum substrate in the form of a frying pan such that dry film thickness of 0.5 mil primer and 0.5 mil topcoat was obtained following a final bake of 427 deg C. (metal temperature) for 3-5 minutes. The resulting baked film was comprised of 33.0 wt % PAI and 38.0 wt % SiC in the primer and 90.3 wt % PTFE and 1.3 wt % PAI in the topcoat layer.

#### Test Results (obtained via the scotch brite egg release test)

Pan	# Cycles	Results
Control 1	<10,000	Exposure of Substrate
Example 1	100,000	Minimal degradation of coating

#### What is claimed is:

1. A non-stick coating formed on a substrate comprising a primer composition and a topcoat composition, wherein said primer composition is between said topcoat composition and said substrate, said primer composition comprising at least one heat resistant adhesion promoter, said topcoat composition comprising at least one fluorocarbon resin and at least one heat resistant adhesion promoter, other than a fluoropolymer that may be the same or different than the adhesion promoter of said primer composition, there being inorganic inert particles with an average particle size of at least about 10 micrometers contained in said primer composition, said primer composition is substantially free of fluorocarbon resin.

2. The coating of claim 1 wherein said fluorocarbon resin comprises one or a mixture of fluorocarbons selected from the group consisting of polytetrafluoroethylene, tetrafluoroethylene, hexafluoropropylene, perfluoropropyl vinyl ether, perfluoroalkyl vinyl ether, perfluoroalkyl vinyl ethylene and co-polymers tetrafluoroethylene-hexafluoropropylene, tetrafluoroethylene-perfluoroalkyl vinyl ether and ethylene-tetrafluoroethylene.

3. The coating of claim 1 wherein said heat resistant adhesion promoter in said primer composition, or in said topcoat composition, or both, is selected from the group consisting of polyamideimide resins, polyethersulfone resins and polyphenylene sulfide resins, or combinations thereof.

4. The coating of claim 3 wherein said heat resistant adhesion promoter in said primer composition, or in said topcoat composition, or both, comprises polyamideimide resin.

5. The coating of claim 1 wherein said topcoat composition comprises from about 1 wt. % to about 20 wt. % adhesion promoter, the wt. % being calculated on basis of the solid content of said topcoat composition.

6. The topcoat composition of claim 5 comprising 55-70 wt. % of a fluorocarbon resin dispersion, 3-10 wt. % of a



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fluorocarbon resin that is flowable at a temperature above about 300° C. and about 5–15 Wt. % of an acrylic resin, the wt. % being calculated on the basis of the solid content of said coating.

7. The coating of claim 1 wherein said topcoat composition comprises at least about 5 wt. % of a fluorocarbon resin that is flowable at a temperature above 300° C.

8. The coating of claim 1 wherein the topcoat composition comprises 55–70 wt. % of a heat stable fluorocarbon resin dispersion, 3–10 wt. % of a fluorocarbon resin that is flowable at a temperature above about 300° C. and 5–15 wt. % of an acrylic resin, the wt. %, being calculated on the basis of the solid content of said topcoat composition.

9. The coating of claim 1 wherein said topcoat composition comprises one or more of components selected from the group comprising an acrylic resin, butyl carbitol, triethanolamine, oleic acid, a hydrocarbon and a cerium based catalyst.

10. The coating of claim 1 comprising an overcoat composition over said topcoat composition.

11. The coating of claim 10 wherein said overcoat composition comprises at least one fluorocarbon resin.

12. The coating of claim 10 wherein said overcoat composition comprises at least one fluorocarbon resin that is flowable at a temperature above about 300° C.

13. The coating of claim 10 wherein said overcoat composition is essentially free of pigments or fillers.

14. The coating of claim 1 wherein said inorganic inert particles are selected from the group consisting of ceramics, inorganic oxides, carbides or nitrides of elements in groups IIA–VB of the periodic table, natural minerals and mixtures thereof.

15. The coating of claim 14 wherein said inorganic inert particles have an average particle size from about 10 to about 80 microns and a Mohs hardness of at least about 5.

16. The coating of claim 15 wherein said inorganic inert particles are selected from the group consisting of alumina,

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zirconia, silicon carbide, titanium carbide, aluminum boride, and cristobalite.

17. The coating of claim 1 wherein said substrate comprises aluminum or aluminum shaped articles.

18. A method of applying a coating to a substrate comprising the sequential steps of:

a. Preparing the surface of said substrate for said coating;

b. Applying a primer composition substantially free of fluorocarbon resin comprising at least one heat resistant adhesion promoter and inorganic inert particles with an average particle size of at least about 10 micrometers;

c. Applying a topcoat composition comprising at least one fluorocarbon resin and at least one heat resistant adhesion promoter other than a fluoropolymer that may be the same or different than the adhesion promoter of said primer composition; and

d. Baking the coated substrate at a temperature from about 380° C. to about 440° C.

19. The method of claim 18 wherein said fluorocarbon resin is applied as a dispersion of said resin in water with a surfactant.

20. The method of claim 18 wherein said fluorocarbon resin is applied as a polymer powder with an organic liquid.

21. The method of claim 18 wherein said primer composition comprises from about 10 wt. % to about 60 wt. % of said adhesion promoter, from about 10 wt. % to about 60 wt. % of said inorganic inert particles and from about 10 wt. % to about 60 wt. % of other ingredients selected from the group consisting of fillers, pigments, surfactants, solvents, defoamers and mixtures thereof, the wt. % being calculated on basis of the solid content of said primer composition.

22. The method of claim 21 wherein said filters are selected from the group consisting of barium sulfate, calcium sulfate, calcium carbonate, silicas and silicates.

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(12) **United States Patent**  
**Bate**

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(54) **NON-STICK COATING AND METHOD OF FORMING SAME**

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(65) **Prior Publication Data**

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**Related U.S. Application Data**

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(51) Int. Cl.<sup>7</sup> ..... **C08L 1/00**

(52) U.S. Cl. .... **524/386; 524/379; 524/502; 524/544; 428/323; 428/422; 428/325; 442/59; 526/89**

(58) Field of Search ..... **524/386, 379, 524/502, 544; 526/89; 428/323, 422, 325, 442; 442/59**

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(57) **ABSTRACT**

Non-stick coatings for use on a flexible substrate include a fluoropolymer, an acrylic polymer, and a polyol and/or diol. The ratio of acrylic polymer to polyol and/or diol is between about 90:10 and about 10:90 by weight, preferably about 50:50. The ratio of acrylic polymer and polyol or diol to fluoropolymer is preferably about 100:60 by weight.

**6 Claims, No Drawings**

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## NON-STICK COATING AND METHOD OF FORMING SAME

This application claims priority to Provisional Application Nos. 60/430,455 filed Dec. 3, 2002 and 60/470,227 filed May 13, 2003.

### BACKGROUND OF THE INVENTION

It is sometimes desirable to coat a flexible surface with a non-stick coating. Traditional coatings that are used on rigid surfaces (e.g. cookware) are unacceptable because they are unable to bend and flex along with the flexible surface. A specific application in which this problem has arisen concerns pressure rollers for printing machines.

Modern printing machines generally contain a heated fuser roller and an opposing pressure roller. As paper is fed between the rollers, the heated fuser roller melts (i.e., fuses) toner onto the paper to form the desired image. The pressure roller applies sufficient pressure to the paper to allow it to touch the fuser roller and have the image applied to it. The pressure roller typically consists of a steel or aluminum core that is coated with some type of rubber. The rubber on the pressure roller is flexible so that it can bend and adapt to the topographical features of the fuser roller and paper. The higher the quality of the image desired, and the faster the printing rate of the printer or copier, the softer the rubber on the pressure roller must be so that the ink does not smudge when it melts. The rubber in modern high quality, high speed printers is commonly a very low durometer silicone rubber. In some copiers, a single roller is capable of acting as the fuser roller, the pressure roller, or both. In addition, some printers apply silicone oil to the roller in order to aid the release of toner.

It is desirable to apply a non-stick coating to the pressure rollers to protect the soft rubber from chemical and thermal degradations, as well as to prevent the paper and ink from sticking to the roller. Applying a non-stick coating to such soft rubber, however, presents a number of problems. First, it is difficult for conventional non-stick coatings to stick to this very soft silicone rubber because the non-stick coating must be able to bend and flex with the silicone rubber that it coats. If the non-stick coating is not sufficiently flexible, it will crack and/or peel away from the pressure roller during use. This decreases the print quality of the resultant image. Second, conventional fluoropolymer coatings are relatively hard when compared to the soft silicone rubbers used on pressure rollers. As a result, the non-stick coatings increase the effective durometer of the pressure roller and decrease the conformability of the roller. This is counterproductive to the goal of a very soft pressure roller that produces a high quality image. Lastly, in those situations where silicone oil is used, the silicone oil can attack the silicone rubber and cause it to swell. Swelling of the silicone rubber is undesirable because it compromises the quality of the image and the life of the roller.

Prior attempts at a non-stick coating for a pressure roller include the application of a fluoropolymer sleeve over the roller surface. Problems with prior art fluoropolymer sleeves, however, include an unacceptable increase in the effective durometer of the pressure roller and a high rate of delaminating due to shear stresses between the fluoropolymer sleeve and the rubber roller. When a sleeve wears out (i.e., delaminates), it peels away from the pressure roller and becomes wrinkled. The wrinkled pressure roller creates very poor quality images and must be replaced at great expense. For this reason, there is a need for non-stick coating that can be used on a flexible surface, yet is durable, functional, and low-cost.

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## BRIEF SUMMARY

A non-stick coating formulation is provided. The coating formulation comprises an acrylic polymer, a polyol or a diol, and a fluoropolymer. The ratio of acrylic polymer to polyol is between about 90:10 and about 10:90 by weight.

### DETAILED DESCRIPTION

The non-stick coating of the present invention may be used to coat a substrate of any desired hardness. The type of substrate to which the coating is applied does not limit the scope of the invention. The coating of the present invention may be used on rigid surfaces (e.g., cookware), though it is preferably used to coat a flexible surface. A "flexible surface" is any surface that deforms, bends, flexes, or changes shape when subjected to an external force or pressure. In one embodiment, the non-stick coating of the present invention is used to coat a soft rubber pressure roller for use in a printing machine, such as a high-speed digital copier or printer. Non-limiting examples of the soft rubbers that may be coated with the non-stick coating of the present invention are silicone rubber, EPDM rubber (ethylene propylene diene rubber), and neoprene.

The non-stick coatings of the present invention may be applied to a substrate in a one-coat process or a multi-coat process. An example of a multi-coat process is a two-coat process consisting of a primer coat and a top coat. The two-coat process results in a coating that is more durable and has better release properties than the one-coat process, however, it may be more expensive.

The non-stick coatings of the present invention contain an acrylic polymer and a diol or a polyol, or mixtures thereof. The ratio of acrylic polymer to diol or polyol is preferably between 90:10 and 10:90 by weight. Generally, the greater the ratio of acrylic polymer to diol or polyol, the stronger but less flexible the resultant coating will be. The preferred ratio of acrylic polymer to diol or polyol therefore depends on the durometer of the substrate being coated and the desired strength of the coating. For example, a ratio of acrylic polymer to diol or polyol of 15:85 or lower is appropriate for a substrate having a durometer less than 10. (Unless otherwise stated, all references to durometer are based on the Shore A scale). For a substrate having a durometer greater than 10, a 50:50 or greater ratio may be used.

Useful acrylic polymers include polymers and copolymers of esters of acrylic acid and methacrylic acid, such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate, butyl methacrylate, and similar monomers. The preferred acrylic polymer is hydroxy-functional. Preferred acrylic polymers are commercially available as an emulsion from S.C. Johnson & Son under the tradename JONCRYL 1540 or as a colloidal dispersion from Noveon Inc. under the tradename CARBOSET 514H. One or more different acrylic polymers may be combined for use in the coating formulations of the present invention. For example, a blend of JONCRYL 1540 and CARBOSET 514H may be used. Such blends are useful to optimize particular characteristics of the coating, such as gloss and chemical resistance.

The coatings of the present invention include a diol, a polyol, or mixtures thereof. As used herein, a diol is any alcohol that contains two hydroxyl groups per molecule and a polyol is any alcohol that contains three or more hydroxyl groups per molecule. Useful diols include urethanes, polyesters, acrylics or hybrid acrylic urethanes. A preferred diol is a polyester diol commercially available from King Industries under the trade name K-FLEX XM 7304. Useful polyols include urethanes, polyesters, acrylics or hybrid acrylic urethanes. A preferred polyol is a polyurethane polyol commercially available from King Industries under the trade name K-FLEX XM 6304.



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Preferably, a melamine is used to cross-link the acrylic polymer with the diol or polyol. A preferred melamine is a methylated melamine formaldehyde resin and is commercially available from Cytec Industries under the tradenames CYMEL 325 or CYMEL 303. Another preferred methylated melamine, hexamethoxymethyl melamine, is commercially available from UCB Inc. under the tradename RESIMENE 745. Desirably, the cross-linking is catalyzed with a blocked acid catalyst. A preferred catalyst is a strong acid catalyst, para-toluene sulfonic acid (P-TSA), commercially available from King Industries under the tradename K-CURE 1040W.

The non-stick coating of the present invention also includes a fluoropolymer. The fluoropolymer is responsible for the non-stick quality of the coating. There are myriad commercially available fluoropolymers and the specific fluoropolymer chosen does not limit the scope of the present invention. The fluoropolymer component of the present invention may include a single type of fluoropolymer, or may include a mixture or blend of more than one type of fluoropolymer. The ratio of acrylic polymer and polyol or diol to fluoropolymer (i.e., (acrylic polymer+polyol/diol):fluoropolymer) is preferably about 100:60 in the formulation for a one-coat system and between about 90:10 and about 70:30 for a formulation intended to be applied as an intermediate coat. Depending on the particular application, it is desirable for the ratio of acrylic polymer and polyol or diol to fluoropolymer in the top coat to be between about 70:30 and about 30:70. A roller that is to be used in a copier that does not use silicone oil preferably includes a top coat having a ratio of acrylic polymer and polyol or diol to fluoropolymer of about 30:70.

Exemplary fluoropolymers are tetrafluoroethylene-perfluoromethyl vinyl ether copolymer (MFA), tetrafluoroethylene-hexafluoropropylene copolymer (FEP), and polytetrafluoroethylene (PTFE). FEP is a preferred fluoropolymer. The preferred FEP is commercially available as a water-based latex dispersion commercially available from Dyneon LLC and sold under the trade name DYNEON FEP X 6300. PTFE is another preferred fluoropolymer. The preferred PTFE is commercially available as a micropowder from Asahi Chemical and sold under the trade name WITCON TL-10.

Non-limiting examples of other acceptable fluoropolymers are polychloro-trifluoroethylene (PCTFE), ethylene-chlorotrifluoroethylene copolymer (ECTFE), ethylene-tetrafluoroethylene copolymer (ETFE), tetrafluoroethylene (TFE) and perfluoro (ethyl vinyl ether) (PEVE) copolymer (PFA), TFE and perfluoro (propyl vinyl ether) (PPVE) copolymer (PFA), polyvinylfluoride (PVF), and polyvinylidene fluoride (PVDF). The fluoropolymer component may also include comonomer modifiers that improve selected characteristics.

The fluoropolymer may be a micropowder. Alternatively, the fluoropolymer may be provided in the form of a dispersion of fluoropolymer in water. By "dispersion" it is meant that the fluoropolymer particles are stably dispersed in water so that the particles do not settle before the dispersion is used. In some cases it may be desirable to include an organic solvent, such as n-methylpyrrolidone, butyrolactone, high boiling aromatic solvents, alcohols, or mixtures thereof.

The coating system of the present invention may include a silane. The silane may be included as an ingredient in a formulation for a one-coat system or applied as the first coat in a multi-coat system. Preferred silanes include vinyltrimethoxysilane, gamma-methacryloxypropyltrimethoxy silane, vinyltris (t-butylperoxy) silane and partially hydrolyzed silanes. The preferred silane for use in a one coat formulation is commercially available from Dowcon under the tradename Z-6020. The silane preferably comprises between 1.0 and

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2.5% by weight of the total non-stick coating formulation. For a multi-coat system, the preferred silane is commercially available from Shin-Etsu Chemical Co. under the tradename X33-156-5. Alternatively, a one-coat formulation containing a silane may be applied as the primer (or other layer) in a multi-coat system.

The coating system of the present invention may include an additive to aid release. The preferred release additive is a polyether modified dimethylpolysiloxane copolymer in a butylglycol solvent that is commercially available from BYK-Chemie GmbH under the tradename BYK-301.

The coating system of the present invention may include a dispersant. The preferred dispersant is an acetylene diol dispersant that is commercially available from Air Products and Chemicals, Inc. under the tradenames SURFYNOL CT 324 or SURFYNOL 104BC.

Following is a specific example of a one-coat formulation. The composition comprises 29.9% acrylic emulsion (43% in water), 2.7% PTFE micropowder, 8.3% propylene glycol, 2.7% alkyl phenol polyethylenoxide, 13.2% polyester diol (30% emulsion in water), 0.3% blocked acid catalyst, 0.9% silane, 0.5% acetylene diol dispersant, and 9.3% methylated melamine formaldehyde resin. The balance of the formulation is water and additives. Each additive comprises less than 2% of the composition. The additives include well known defoamers, flow agents, dispersants, surfactants, stabilizers, thickeners and/or fillers.

The one-coat formulation is filtered through a mesh filter rated at 53 microns and sprayed onto the substrate by conventional or high volume, low pressure (HVLP) methods. The thickness of the dry coat is from about 20 to about 30 microns.

The coating is cured for about ten minutes in a conventional oven operating at approximate 450° F. The silicone rubber that is commonly used to coat pressure rollers begins to thermally decompose at about 500–550° F. Thus, it is desirable to cure the coating in such a manner that the temperature of the silicone rubber stays below 500° F.

As noted above, the non-stick coating of the present invention can be applied in a two-coat process. The first coat is a primer that helps bond a subsequent layer which contains a fluoropolymer to the substrate. Any primer that effectively bonds to the chosen substrate is acceptable. Where the substrate consists of silicone rubber or other rubber having a hydroxy functional group (such as EPDM rubber), the primer is preferably a silane primer as described above. The primer component may consist of a single type of primer; alternatively, different primers may be mixed or combined to form the primer. The primer is preferably applied as a very thin layer having a thickness of between one molecule to a few microns. The primer may be applied by wiping it on the substrate with a cloth or by conventional or HVLP spray guns. The applied primer is typically very volatile and may be dried by any desirable means, though it is preferably dried in a conventional oven at 150° F. for about 3–5 minutes or at air temperature (–77° F.) for about fifteen minutes.

A first embodiment of a top coat composition comprises 23.0% acrylic polymer emulsion (43% in water), 13.1% PTFE micropowder, 6.5% propylene glycol, 2.1% alkyl phenol polyethylenoxide, 10.2% polyurethane diol (30% emulsion in water), 1% silane, 0.5% acetylene diol dispersant, and 0.3% blocked acid catalyst. The balance of the formulation is water and additives. Each additive comprises less than 2% of the composition. The additives include well known defoamers, flow agents, dispersants, surfactants, stabilizers, thickeners and/or fillers. This composition has a ratio of acrylic polymer to diol of about 85:15 and a ratio of acrylic polymer and polyol to fluoropolymer of about 70:30.

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A second embodiment of a top coat composition comprises approximately 7% acrylic polymer emulsion, 22% polyurethane polyol, 7.1% methylated melamine formaldehyde resin, 17.8% FEP dispersion, 0.3% blocked acid catalyst, 6.7% propylene glycol, and 5% of a polyether modified dimethylpolysiloxane copolymer release agent. The balance of the formulation is water and additives. Each additive comprises less than 2% of the composition. The additives include well known defoamers, flow agents, dispersants, surfactants, stabilizers, thickeners and/or fillers. This composition has a ratio of acrylic to polyol of about 85:15 and a ratio of acrylic polymer and polyol to fluoropolymer of about 70:30. This embodiment of a top coat is particularly useful where the coated roller may come in contact with silicone oil.

The preferred thickness of the top coat varies according to the hardness of the substrate. If the durometer of the substrate is less than 10, the thickness of the top coat is preferably less than 5 microns. If the durometer of the substrate is between 10 and 20, the thickness of the top coat is preferably less than 7 microns. If the durometer of the substrate is greater than 20, the thickness of the top coat is preferably greater than 10 microns, most preferably about 20-30 microns. The top coat is sprayed directly on top of the dried primer and the article is cured in a conventional oven at about 400° F. for about 10 minutes. If the coating is to be used in a copier that uses silicone oil, it is desirable to cure the coating at a lower temperature, e.g., about 350° F. The lower temperature is preferred in order to avoid the formation of a completely melted, continuous network of fluoropolymer. A discontinuous network of fluoropolymer is preferred because it creates interstices that absorb silicone oil and aid efficient operation of the copier.

In another embodiment, the non-stick coating of the present invention can be applied in a three-step process. The first coat is a primer that helps bond a subsequent layer which contains a fluoropolymer to the substrate. Any primer that effectively bonds to the chosen substrate is acceptable. Where the substrate consists of silicone rubber or other rubber having a hydroxy functional group (such as EPDM rubber), the primer is preferably a silane primer as described above. The primer component may consist of a single type of primer; alternatively, different primers may be mixed or combined to form the primer. The primer is preferably applied as a very thin layer having a thickness of between one molecule to a few microns. The primer may be applied by wiping it on the substrate with a cloth or by conventional or HVLP spray guns. The applied primer is typically very volatile and may be dried by any desirable means, though it is preferably dried in a conventional oven at 150° F. for about 3-5 minutes or at air temperature (~77° F.) for about fifteen minutes.

The first embodiment of a top coat described above with respect to the two-coat process is an acceptable mid-coat for the three-coat process. Another embodiment of a mid-coat composition comprises approximately 7% acrylic polymer emulsion, 22% polyurethane polyol, 7.1% methylated melamine formaldehyde resin, 17.8% FEP dispersion, 0.5% acetylene diol dispersant, 0.3% blocked acid catalyst, and 6.7% propylene glycol. The balance of the formulation is water and additives. Each additive comprises less than 2% of the composition. The additives include well known defoamers, flow agents, dispersants, surfactants, stabilizers, thickeners and/or fillers. This composition has a ratio of acrylic to polyol of about 85:15 and a ratio of acrylic and polyol to fluoropolymer of about 70:30.

A preferred top coat for the three-coat process further includes a release additive and a higher percentage of

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fluoropolymer. The preferred top coat composition comprises approximately 4.1% acrylic polymer emulsion, 12.3% polyurethane polyol, 3.8% polypropylene glycol, 3.9% methylated melamine formaldehyde resin, 53.9% FEP dispersion, and 5.7% of a release additive, such as a polyether modified dimethylpolysiloxane copolymer. The composition has a ratio of acrylic polymer to diol of about 85:15 and a ratio of acrylic polymer and polyol to fluoropolymer of about 30:70.

The three-coat system described above is cured at about 550° F. for about 10 minutes. It is desirable to cure the system at a sufficient temperature, and for a sufficient time, to melt the fluoropolymer into a continuous network.

Any of the coatings described herein can be made to be conductive. In high-speed copiers it is very easy for a large static charge to build up in the paper and to compromise image quality. For this reason, it may be desirable to have a conductive coating that dissipates the static charge. The coatings discussed above may be made conductive by the addition of an electrically conductive pigment such as KETJEN BLACK, which is commercially available from Akzo-Nobel Coating Inc.

Specific one-coat and two-coat embodiments are provided above, however, the number of coats employed does not limit the scope of the present invention. Non-stick coatings of the present invention may also consist of three or more coats. For example, it may be desirable to use two different primers or it may be desirable to add one or more intermediate coats.

While particular embodiments of the present invention have been illustrated and described above, the present invention should not be limited to such examples and descriptions. It should be apparent that changes and modifications may be incorporated and embodied as part of the present invention within the scope of the following claims.

What is claimed is:

1. A non-stick coating formulation comprising:

- a. an acrylic polymer,
- b. an alcohol selected from the group consisting of a polyurethane polyol, a polyester diol, and mixtures thereof, and
- c. a fluoropolymer; wherein the ratio of acrylic polymer to the alcohol is between about 90:10 and about 10:90 by weight.

2. The non-stick coating formulation of claim 1, wherein the alcohol is a polyester diol.

3. The non-stick coating formulation of claim 1, wherein the alcohol is a polyurethane polyol.

4. A non-stick coating formulation comprising:

- a. an acrylic polymer,
- b. an alcohol selected from the group consisting of a diol, a polyol, and mixtures thereof,
- c. a fluoropolymer, and
- d. a polyether modified dimethylpolysiloxane copolymer wherein the ratio of acrylic polymer to the alcohol is between about 90:10 and about 10:90 by weight.

5. The non-stick coating formulation of claim 4, wherein the ratio of acrylic polymer to the alcohol is about 70:30 by weight.

6. The non-stick coating formulation of claim 4, wherein the ratio of acrylic polymer to the alcohol is about 30:70 by weight.

\* \* \* \* \*

## USPTO PATENT FULL-TEXT AND IMAGE DATABASE

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( 1 of 1 )

**United States Patent**

**7,375,152**

**Bate**

**May 20, 2008**

Non-stick coating and method of forming same

### Abstract

Non-stick coatings for use on a flexible substrate include a fluoropolymer, an acrylic polymer, and a polyol and/or diol. The ratio of acrylic polymer to polyol and/or diol is between about 90:10 and about 10:90 by weight, preferably about 50:50. The ratio of acrylic polymer and polyol or diol to fluoropolymer is preferably about 100:60 by weight.

Inventors: **Bate; Thomas J.** (Glenview, IL)

Assignee: **Akzo Nobel Non-Stick Coatings** (Des Plaines, IL)

Appl. No.: **11/153,289**

Filed: **June 15, 2005**

### Related U.S. Patent Documents

<u>Application Number</u>	<u>Filing Date</u>	<u>Patent Number</u>	<u>Issue Date</u>
10727791	Dec., 2003	6921787	
60430455	Dec., 2002		
60470227	May., 2003		

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524/386 ; 428/323; 428/325; 428/422; 442/59; 524/379;  
524/502; 524/544; 526/89

**Current International Class:**

C08L 1/00 (20060101)

**Field of Search:**

524/386,379,502,544 526/89 428/323,422,325 442/59

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*Assistant Examiner:* Hu; Henry

*Attorney, Agent or Firm:* Brinks Hofer Gilson & Lione

#### Parent Case Text

#### CROSS-REFERENCE TO RELATED PATENTS

This is a divisional of application Ser. No. 10/727,791, filed Dec. 3, 2003, now U.S. Pat. No. 6,921,787, which is a continuing application of Ser. Nos. 60/430,455 filed Dec. 3, 2002 and 60/470,227 filed May 13, 2003.

#### Claims

The invention claimed is:

1. A non-stick coating formulation comprising: a. an acrylic polymer, b. an alcohol selected from the group consisting of a diol, a polyol, and mixtures thereof, and c. a fluoropolymer, and d. a cross-linking agent for cross-linking the acrylic polymer with the alcohol; wherein the alcohol comprises a polyurethane polyol.
2. A non-stick coating formulation comprising: a. an acrylic polymer, b. an alcohol selected from the group consisting of a diol, a polyol, and mixtures thereof, and c. a fluoropolymer, d. a cross-linking agent for cross-linking the acrylic polymer with the alcohol, and e. a polyether modified dimethylpolysiloxane copolymer.



3. A non-stick coating formulation comprising: a. an acrylic polymer, b. an alcohol selected from the group consisting of a diol, a polyol, and mixtures thereof, and c. a fluoropolymer, and d. a cross-linking agent for cross-linking the acrylic polymer with the alcohol, and e. a blocked acid catalyst.

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### *Description*

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## BACKGROUND OF THE INVENTION

It is sometimes desirable to coat a flexible surface with a non-stick coating. Traditional coatings that are used on rigid surfaces (e.g. cookware) are unacceptable because they are unable to bend and flex along with the flexible surface. A specific application in which this problem has arisen concerns pressure rollers for printing machines.

Modern printing machines generally contain a heated fuser roller and an opposing pressure roller. As paper is fed between the rollers, the heated fuser roller melts (i.e., fuses) toner onto the paper to form the desired image. The pressure roller applies sufficient pressure to the paper to allow it to touch the fuser roller and have the image applied to it. The pressure roller typically consists of a steel or aluminum core that is coated with some type of rubber. The rubber on the pressure roller is flexible so that it can bend and adapt to the topographical features of the fuser roller and paper. The higher the quality of the image desired, and the faster the printing rate of the printer or copier, the softer the rubber on the pressure roller must be so that the ink does not smudge when it melts. The rubber in modern high quality, high speed printers is commonly a very low durometer silicone rubber. In some copiers, a single roller is capable of acting as the fuser roller, the pressure roller, or both. In addition, some printers apply silicone oil to the roller in order to aid the release of toner.

It is desirable to apply a non-stick coating to the pressure rollers to protect the soft rubber from chemical and thermal degradations, as well as to prevent the paper and ink from sticking to the roller. Applying a non-stick coating to such soft rubber, however, presents a number of problems. First, it is difficult for conventional non-stick coatings to stick to this very soft silicone rubber because the non-stick coating must be able to bend and flex with the silicone rubber that it coats. If the non-stick coating is not sufficiently flexible, it will crack and/or peel away from the pressure roller during use. This decreases the print quality of the resultant image. Second, conventional fluoropolymer coatings are relatively hard when compared to the soft silicone rubbers used on pressure rollers. As a result, the non-stick coatings increase the effective durometer of the pressure roller and decrease the conformability of the roller. This is counterproductive to the goal of a very soft pressure roller that produces a high quality image. Lastly, in those situations where silicone oil is used, the silicone oil can attack the silicone rubber and cause it to swell. Swelling of the silicone rubber is undesirable because it compromises the quality of the image and the life of the roller.

Prior attempts at a non-stick coating for a pressure roller include the application of a fluoropolymer sleeve over the roller surface. Problems with prior art fluoropolymer sleeves, however, include an unacceptable increase in the effective durometer of the pressure roller and a high rate of delaminating due to shear stresses between the fluoropolymer sleeve and the rubber roller. When a sleeve wears out (i.e., delaminates), it peels away from the pressure roller and becomes wrinkled. The wrinkled pressure roller creates very poor quality images and must be replaced at great expense. For this reason, there is a need for non-stick coating that can be used on a flexible surface, yet is durable, functional, and low-cost.

## BRIEF SUMMARY



A non-stick coating formulation is provided. The coating formulation comprises an acrylic polymer, a polyol or a diol, and a fluoropolymer. The ratio of acrylic polymer to polyol is between about 90:10 and about 10:90 by weight.

## DETAILED DESCRIPTION

The non-stick coating of the present invention may be used to coat a substrate of any desired hardness. The type of substrate to which the coating is applied does not limit the scope of the invention. The coating of the present invention may be used on rigid surfaces (e.g., cookware), though it is preferably used to coat a flexible surface. A "flexible surface" is any surface that deforms, bends, flexes, or changes shape when subjected to an external force or pressure. In one embodiment, the non-stick coating of the present invention is used to coat a soft rubber pressure roller for use in a printing machine, such as a high-speed digital copier or printer. Non-limiting examples of the soft rubbers that may be coated with the non-stick coating of the present invention are silicone rubber, EPDM rubber (ethylene propylene diene rubber), and neoprene.

The non-stick coatings of the present invention may be applied to a substrate in a one-coat process or a multi-coat process. An example of a multi-coat process is a two-coat process consisting of a primer coat and a top coat. The two-coat process results in a coating that is more durable and has better release properties than the one-coat process, however, it may be more expensive.

The non-stick coatings of the present invention contain an acrylic polymer and a diol or a polyol, or mixtures thereof. The ratio of acrylic polymer to diol or polyol is preferably between 90:10 and 10:90 by weight. Generally, the greater the ratio of acrylic polymer to diol or polyol, the stronger but less flexible the resultant coating will be. The preferred ratio of acrylic polymer to diol or polyol therefore depends on the durometer of the substrate being coated and the desired strength of the coating. For example, a ratio of acrylic polymer to diol or polyol of 15:85 or lower is appropriate for a substrate having a durometer less than 10. (Unless otherwise stated, all references to durometer are based on the Shore A scale). For a substrate having a durometer greater than 10, a 50:50 or greater ratio may be used.

Useful acrylic polymers include polymers and copolymers of esters of acrylic acid and methacrylic acid, such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate, butyl methacrylate, and similar monomers. The preferred acrylic polymer is hydroxy-functional. Preferred acrylic polymers are commercially available as an emulsion from S.C. Johnson & Son under the tradename JONCRYL 1540 or as a colloidal dispersion from Noveon Inc. under the tradename CARBOSET 514H. One or more different acrylic polymers may be combined for use in the coating formulations of the present invention. For example, a blend of JONCRYL 1540 and CARBOSET 514H may be used. Such blends are useful to optimize particular characteristics of the coating, such as gloss and chemical resistance.

The coatings of the present invention include a diol, a polyol, or mixtures thereof. As used herein, a diol is any alcohol that contains two hydroxyl groups per molecule and a polyol is any alcohol that contains three or more hydroxyl groups per molecule. Useful diols include urethanes, polyesters, acrylics or hybrid acrylic urethanes. A preferred diol is a polyester diol commercially available from King Industries under the trade name K-FLEX XM 7304. Useful polyols include urethanes, polyesters, acrylics or hybrid acrylic urethanes. A preferred polyol is a polyurethane polyol commercially available from King Industries under the trade name K-FLEX XM 6304.

Preferably, a melamine is used to cross-link the acrylic polymer with the diol or polyol. A preferred melamine is a methylated melamine formaldehyde resin and is commercially available from Cytec

Industries under the tradenames CYMEL 325 or CYMEL 303. Another preferred methylated melamine, hexamethoxymethyl melamine, is commercially available from UCB Inc. under the tradename RESIMENE 745. Desirably, the cross-linking is catalyzed with a blocked acid catalyst. A preferred catalyst is a strong acid catalyst, para-toluene sulfonic acid (P-TSA), commercially available from King Industries under the tradename K-CURE 1040W.

The non-stick coating of the present invention also includes a fluoropolymer. The fluoropolymer is responsible for the non-stick quality of the coating. There are myriad commercially available fluoropolymers and the specific fluoropolymer chosen does not limit the scope of the present invention. The fluoropolymer component of the present invention may include a single type of fluoropolymer, or may include a mixture or blend of more than one type of fluoropolymer. The ratio of acrylic polymer and polyol or diol to fluoropolymer (i.e., (acrylic polymer+polyol/diol):fluoropolymer) is preferably about 100:60 in the formulation for a one-coat system and between about 90:10 and about 70:30 for a formulation intended to be applied as an intermediate coat. Depending on the particular application, it is desirable for the ratio of acrylic polymer and polyol or diol to fluoropolymer in the top coat to be between about 70:30 and about 30:70. A roller that is to be used in a copier that does not use silicone oil preferably includes a top coat having a ratio of acrylic polymer and polyol or diol to fluoropolymer of about 30:70.

Exemplary fluoropolymers are tetrafluoroethylene-perfluoromethyl vinyl ether copolymer (MFA), tetrafluoroethylene-hexafluoropropylene copolymer (FEP), and polytetrafluoroethylene (PTFE). FEP is a preferred fluoropolymer. The preferred FEP is commercially available as a water-based latex dispersion commercially available from Dyneon LLC and sold under the trade name DYNEON FEP X 6300. PTFE is another preferred fluoropolymer. The preferred PTFE is commercially available as a micropowder from Asahi Chemical and sold under the trade name WITCON TL-10.

Non-limiting examples of other acceptable fluoropolymers are polychloro-trifluoroethylene (PCTFE), ethylene-chlorotrifluoroethylene copolymer (ECTFE), ethylene-tetrafluoroethylene copolymer (ETFE), tetrafluoroethylene (TFE) and perfluoro (ethyl vinyl ether) (PEVE) copolymer (PFA), TFE and perfluoro (propyl vinyl ether) (PPVE) copolymer (PFA), polyvinylfluoride (PVF), and polyvinylidene fluoride (PVDF). The fluoropolymer component may also include comonomer modifiers that improve selected characteristics.

The fluoropolymer may be a micropowder. Alternatively, the fluoropolymer may be provided in the form of a dispersion of fluoropolymer in water. By "dispersion" it is meant that the fluoropolymer particles are stably dispersed in water so that the particles do not settle before the dispersion is used. In some cases it may be desirable to include an organic solvent, such as n-methylpyrrolidone, butyrolactone, high boiling aromatic solvents, alcohols, or mixtures thereof.

The coating system of the present invention may include a silane. The silane may be included as an ingredient in a formulation for a one-coat system or applied as the first coat in a multi-coat system. Preferred silanes include vinyltrimethoxysilane, gamma-methacycloxypropyltrimethoxy silane, vinyltris (t-butylperoxy) silane and partially hydrolyzed silanes. The preferred silane for use in a one coat formulation is commercially available from Dowcon under the tradename Z-6020. The silane preferably comprises between 1.0 and 2.5% by weight of the total non-stick coating formulation. For a multi-coat system, the preferred silane is commercially available from Shin-Etsu Chemical Co. under the tradename X33-156-5. Alternatively, a one-coat formulation containing a silane may be applied as the primer (or other layer) in a multi-coat system.

The coating system of the present invention may include an additive to aid release. The preferred release additive is a polyether modified dimethylpolysiloxane copolymer in a butylglycol solvent that is

commercially available from BYK-Chemie GmbH under the tradename BYK-301.

The coating system of the present invention may include a dispersant. The preferred dispersant is an acetylene diol dispersant that is commercially available from Air Products and Chemicals, Inc. under the tradenames SURFYNOL CT 324 or SURFYNOL 104BC.

Following is a specific example of a one-coat formulation. The composition comprises 29.9% acrylic emulsion (43% in water), 2.7% PTFE micropowder, 8.3% propylene glycol, 2.7% alkyl phenol polyethelyeneoxide, 13.2% polyester diol (30% emulsion in water), 0.3% blocked acid catalyst, 0.9% silane, 0.5% acetylene diol dispersant, and 9.3% methylated melamine formaldehyde resin. The balance of the formulation is water and additives. Each additive comprises less than 2% of the composition. The additives include well known defoamers, flow agents, dispersants, surfactants, stabilizers, thickeners and/or fillers.

The one-coat formulation is filtered through a mesh filter rated at 53 microns and sprayed onto the substrate by conventional or high volume, low pressure (HVLP) methods. The thickness of the dry coat is from about 20 to about 30 microns.

The coating is cured for about ten minutes in a conventional oven operating at approximate 450.degree. F. The silicone rubber that is commonly used to coat pressure rollers begins to thermally decompose at about 500-550.degree. F. Thus, it is desirable to cure the coating in such a manner that the temperature of the silicone rubber stays below 500.degree. F.

As noted above, the non-stick coating of the present invention can be applied in a two-coat process. The first coat is a primer that helps bond a subsequent layer which contains a fluoropolymer to the substrate. Any primer that effectively bonds to the chosen substrate is acceptable. Where the substrate consists of silicone rubber or other rubber having a hydroxy functional group (such as EPDM rubber), the primer is preferably a silane primer as described above. The primer component may consist of a single type of primer; alternatively, different primers may be mixed or combined to form the primer. The primer is preferably applied as a very thin layer having a thickness of between one molecule to a few microns. The primer may be applied by wiping it on the substrate with a cloth or by conventional or HVLP spray guns. The applied primer is typically very volatile and may be dried by any desirable means, though it is preferably dried in a conventional oven at 150.degree. F. for about 3-5 minutes or at air temperature (about 77.degree. F.) for about fifteen minutes.

A first embodiment of a top coat composition comprises 23.0% acrylic polymer emulsion (43% in water), 13.1% PTFE micropowder, 6.5% propylene glycol, 2.1% alkyl phenol polyethelyeneoxide, 10.2% polyurethane diol (30% emulsion in water), 1% silane, 0.5% acetylene diol dispersant, and 0.3% blocked acid catalyst. The balance of the formulation is water and additives. Each additive comprises less than 2% of the composition. The additives include well known defoamers, flow agents, dispersants, surfactants, stabilizers, thickeners and/or fillers. This composition has a ratio of acrylic polymer to diol of about 85:15 and a ratio of acrylic polymer and polyol to fluoropolymer of about 70:30.

A second embodiment of a top coat composition comprises approximately 7% acrylic polymer emulsion, 22% polyurethane polyol, 7.1% methylated melamine formaldehyde resin, 17.8% FEP dispersion, 0.3% blocked acid catalyst, 6.7% propylene glycol, and 5% of a polyether modified dimethylpolysiloxane copolymer release agent. The balance of the formulation is water and additives. Each additive comprises less than 2% of the composition. The additives include well known defoamers, flow agents, dispersants, surfactants, stabilizers, thickeners and/or fillers. This composition has a ratio of acrylic to polyol of about 85:15 and a ratio of acrylic polymer and polyol to fluoropolymer of about 70:30. This embodiment of a top coat is particularly useful where the coated roller may come in contact



with silicone oil.

The preferred thickness of the top coat varies according to the hardness of the substrate. If the durometer of the substrate is less than 10, the thickness of the top coat is preferably less than 5 microns. If the durometer of the substrate is between 10 and 20, the thickness of the top coat is preferably less than 7 microns. If the durometer of the substrate is greater than 20, the thickness of the top coat is preferably greater than 10 microns, most preferably about 20-30 microns. The top coat is sprayed directly on top of the dried primer and the article is cured in a conventional oven at about 400.degree. F. for about 10 minutes. If the coating is to be used in a copier that uses silicone oil, it is desirable to cure the coating at a lower temperature, e.g., about 350.degree. F. The lower temperature is preferred in order to avoid the formation of a completely melted, continuous network of fluoropolymer. A discontinuous network of fluoropolymer is preferred because it creates interstices that absorb silicone oil and aid efficient operation of the copier.

In another embodiment, the non-stick coating of the present invention can be applied in a three-step process. The first coat is a primer that helps bond a subsequent layer which contains a fluoropolymer to the substrate. Any primer that effectively bonds to the chosen substrate is acceptable. Where the substrate consists of silicone rubber or other rubber having a hydroxy functional group (such as EPDM rubber), the primer is preferably a silane primer as described above. The primer component may consist of a single type of primer; alternatively, different primers may be mixed or combined to form the primer. The primer is preferably applied as a very thin layer having a thickness of between one molecule to a few microns. The primer may be applied by wiping it on the substrate with a cloth or by conventional or HVLP spray guns. The applied primer is typically very volatile and may be dried by any desirable means, though it is preferably dried in a conventional oven at 150.degree. F. for about 3-5 minutes or at air temperature (about .degree. F.) for about fifteen minutes.

The first embodiment of a top coat described above with respect to the two-coat process is an acceptable mid-coat for the three-coat process. Another embodiment of a mid-coat composition comprises approximately 7% acrylic polymer emulsion, 22% polyurethane polyol, 7.1% methylated melamine formaldehyde resin, 17.8% FEP dispersion, 0.5% acetylene diol dispersant, 0.3% blocked acid catalyst, and 6.7% propylene glycol. The balance of the formulation is water and additives. Each additive comprises less than 2% of the composition. The additives include well known defoamers, flow agents, dispersants, surfactants, stabilizers, thickeners and/or fillers. This composition has a ratio of acrylic to polyol of about 85:15 and a ratio of acrylic and polyol to fluoropolymer of about 70:30.

A preferred top coat for the three-coat process further includes a release additive and a higher percentage of fluoropolymer. The preferred top coat composition comprises approximately 4.1% acrylic polymer emulsion, 12.3% polyurethane polyol, 3.8% polypropylene glycol, 3.9% methylated melamine formaldehyde resin, 53.9% FEP dispersion, and 5.7% of a release additive, such as a polyether modified dimethylpolysiloxane copolymer. The composition has a ratio of acrylic polymer to diol of about 85:15 and a ratio of acrylic polymer and polyol to fluoropolymer of about 30:70.

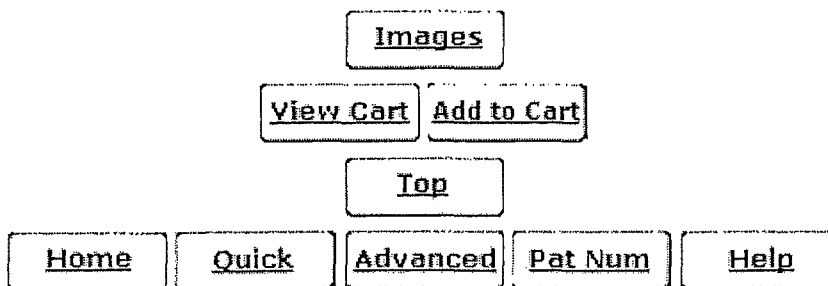
The three-coat system described above is cured at about 550.degree. F. for about 10 minutes. It is desirable to cure the system at a sufficient temperature, and for a sufficient time, to melt the fluoropolymer into a continuous network.

Any of the coatings described herein can be made to be conductive. In high-speed copiers it is very easy for a large static charge to build up in the paper and to compromise image quality. For this reason, it may be desirable to have a conductive coating that dissipates the static charge. The coatings discussed above may be made conductive by the addition of an electrically conductive pigment such as KETJEN BLACK, which is commercially available from Akzo-Nobel Coating Inc.

Specific one-coat and two-coat embodiments are provided above, however, the number of coats employed does not limit the scope of the present invention. Non-stick coatings of the present invention may also consist of three or more coats. For example, it may be desirable to use two different primers or it may be desirable to add one or more intermediate coats.

While particular embodiments of the present invention have been illustrated and described above, the present invention should not be limited to such examples and descriptions. It should be apparent that changes and modifications may be incorporated and embodied as part of the present invention within the scope of the following claims.

\* \* \* \* \*







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**Bate**

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(54) **ELECTRICALLY CONDUCTIVE NON-STICK COATING**

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**C08L 23/00** (2006.01)

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See application file for complete search history.

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(57) **ABSTRACT**

A non-stick coating includes fluoropolymer and electrically conductive mica. The coating may be used on rollers in printing machines to help dissipate static electricity.

**6 Claims, No Drawings**

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ELECTRICALLY CONDUCTIVE NON-STICK  
COATING

## BACKGROUND OF THE INVENTION

Modern printing machines generally contain a heated fuser roller and an opposing pressure roller. As paper is fed between the rollers, the heated fuser roller melts (i.e., fuses) toner onto the paper to form the desired image. The pressure roller applies sufficient pressure to the paper to allow it to touch the fuser roller and have the image applied to it. The fuser roller typically consists of a steel or aluminum core. The pressure roller typically also consists of a steel or aluminum core, but further includes a flexible rubber coating that can bend and adapt to the topographical features of the fuser roller and paper.

Rollers in copiers and printers can built up a static charge that compromises image quality and printing speed. Static electricity can be particularly problematic with fuser rollers. For this reason, it is sometimes desirable for a non-stick coating on a roller to be electrically conductive and have the ability to dissipate static electricity. Prior coatings were commonly made conductive by including carbon black. Such coatings, however, may include such a large volume of carbon black that the carbon black compromises the non-stick characteristics of the coating and limits the ability to have a conductive non-stick coating that is any color other than black. An improved conductive non-stick coating is therefore desired.

## BRIEF SUMMARY OF THE INVENTION

The non-stick coating of the present invention includes fluoropolymer and electrically conductive mica.

A method of dissipating static electricity in a printing machine roller is also provided. The method comprises the steps of providing a printing machine roller, coating the printing machine roller with a non-stick coating that includes fluoropolymer and electrically conductive mica, curing the coating on the printing machine roller, and installing the printing machine roller in the printing machine.

DETAILED DESCRIPTION OF THE  
PREFERRED EMBODIMENTS

The non-stick coating of the present invention may be used to coat a substrate of any desired hardness. The type of substrate to which the coating is applied does not limit the scope of the invention. In one embodiment, the non-stick coating of the present invention is used to coat a roller for use in a printing machine, such as a high-speed digital copier or printer. The roller may be a pressure roller or a fuser roller. Most preferably, the coating of the present invention is used to coat a fuser roller. As used herein, "roller" refers generally to pressure rollers, fuser rollers, and the like, unless specifically stated otherwise.

The non-stick coating of the present invention may be applied as a one-coat system or as part of a multi-coat system. By way of example, a multi-coat system may consist of a base coat and a top coat. Alternatively, one or more intermediate coatings may be applied between the base coat and the top coat. In a preferred embodiment, the non-stick coating of the present invention is applied as the top coat in a two-coat system. The non-stick coatings of the present invention can be used, however, as any one of the coats in a multi-coat system.

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The non-stick coatings of the present invention include electrically conductive mica. "Electrically conductive mica" is mica that has been treated to create an electrically conductive material. Examples of electrically conductive mica include, but are not limited to, mica that has been coated with conductive metals, conductive metal oxides, conductive polymers, and/or materials that contain conductive metals, metal oxides and/or polymers. Exemplary, non-limiting examples of metal oxides that can be used to coat the mica are indium oxide, tin antimony oxide, titanium dioxide, and/or tin dioxide. Preferably, the mica that is coated is in flat, platelet form. The mica may be natural or synthetic. The preferred electrically conductive mica comprises flat platelets of mica coated with tin antimony oxide (tin oxide doped with antimony) and is commercially available from EM Industries, Inc. under the trade name MINATEC 40CM.

As discussed above, it is preferred that the coated mica is in platelet form. Alternatively, the mica may be in the form of long fibers. An exemplary fibrous electrically conductive mica is 3M Metal Coated Particles SD220 which is commercially available from 3M Corporation. When fibrous mica is incorporated in a non-stick coating, the long strands of mica may extend out of the coating. If the coating containing the fibrous mica is a base or intermediate coat, the fibrous mica may reach into adjacent coating(s). It is preferred that fibrous mica is used in a base coat or intermediate coat to create a conductive bridge between and within different layers. This conductive bridge enhances the ability of a multi-coat system to dissipate static electricity. A base coat or intermediate coat that includes fibrous electrically conductive mica is preferably used with a top coat that includes electrically conductive mica in platelet form.

Fibrous conductive mica is also useful in a base or intermediate coat where a particular overall color is desired for the multi-coat system. Carbon black is commonly used in base or intermediate coats, but, in situations where the base or intermediate coats include carbon black, the overall color of the coating is generally also black because the deep black color of the carbon black dominates the presence of any other colors. Use of fibrous conductive mica instead of carbon black enables different colored coatings (i.e. coatings that are not black) because the fibrous conductive mica does not dominate the color of the coating to the same extent as carbon black. As a result, the benefit of non-black pigments may be fully realized in a conductive non-stick coating.

The non-stick coatings of the present invention may include one or more different electrically conductive micas. The particle size of the electrically conductive mica should be the size that is appropriate for the particular application. The particle size of electrically conductive mica in platelet form is preferably about 1 to 20 microns, and most preferably about 5 to 10 microns. An appropriate amount of electrically conductive mica should be used for the particular application. Generally, the preferred amount of electrically conductive mica is about 0.1% to 10% by weight, preferably about 0.5 to 5% by weight, and most preferably about 1% by weight. In general, the amount of electrically conductive mica that is required for a particular application occupies less volume in the coating and facilitates better release and color characteristics for the coating than prior conductive pigments such as carbon black. As used herein, weight percentages are expressed as a percent of the wet coating formulation.

The non-stick coating of the present invention includes fluoropolymer. The fluoropolymer is responsible for the non-stick quality of the coating. There are myriad commer-

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cially available fluoropolymers and the specific fluoropolymer chosen does not limit the scope of the present invention. The fluoropolymer component of the present invention may include a single type of fluoropolymer, or may include a mixture or blend of more than one type of fluoropolymer. The fluoropolymer may be a micropowder or a dispersion of fluoropolymer in water. By "dispersion" it is meant that the fluoropolymer particles are stably dispersed in water so that the particles do not settle before the dispersion is used. In some cases it may be desirable to include an organic solvent, such as n-methylpyrrolidone, butyrolactone, high boiling aromatic solvents, alcohols, or mixtures thereof. The fluoropolymer used in the coating of the present invention is preferably provided a dispersion.

Exemplary fluoropolymers are tetrafluoroethylene-perfluoromethyl vinyl ether copolymer (MFA), tetrafluoroethylene-hexafluoropropylene copolymer (FEP), and polytetrafluoroethylene (PTFE). Non-limiting examples of other acceptable fluoropolymers are polychloro-trifluoroethylene (PCTFE), ethylene-chlorotrifluoroethylene copolymer (ECTFE), ethylene-tetrafluoroethylene copolymer (BTFE), tetrafluoroethylene (TFE) and perfluoro (ethyl vinyl ether) (PEVE) copolymer (PFA), TFE and perfluoro (propyl vinyl ether) (PPVE) copolymer (PFA), polyvinylfluoride (PVF), and polyvinylidene fluoride (PVDF). The fluoropolymer component may also include comonomer modifiers that improve selected characteristics.

PTFE and PFA are the preferred fluoropolymers. The preferred PTFE is commercially available as a dispersion from Daikin America, Inc. and sold under the trade name DAIKIN-POLYFLON. The preferred PFA is commercially available as a dispersion from 3M and sold under the trade name DYNEON PFA 6900 N.

The coating of the present invention may include an acrylic polymer. Useful acrylic polymers include polymers and copolymers of esters of acrylic acid and methacrylic acid, such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate, butyl methacrylate, and similar monomers. One or more different acrylic polymers may be combined for use in the coating formulations of the present invention. A preferred acrylic polymer is commercially available from Zeneca, Inc. under the trade name NEOCRYL BT 44

The wet non-stick coating formulation of the present invention can be sprayed onto a substrate, such as a steel or aluminum fuser roller in a printing machine, by conventional or high volume, low pressure (HVLP) methods. The substrate may already include one or more coatings. The thickness of any existing coatings is preferably less than 10 microns. The coating of the present invention is applied to the substrate and is preferably cured for 5 minutes at 820° F.

The solvent system and the drying time used with the coating of the present invention are preferably chosen so that the time to cure the coating is sufficiently long for the mica particles to orient themselves. For example, if the electrically conductive mica comprises flat platelets of coated mica, it is preferred that the coating is cured for a time that is long enough for the platelets of mica to orient themselves in a generally horizontal relationship with respect to the substrate. The thickness of the coating of the present invention after it has been cured is preferably about 5 to about 15 microns, most preferably about 10 microns.

In a preferred embodiment, the coating is applied to a fuser roller for use in a printing machine. The conductive,

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non-stick coating on the installed fuser roller helps dissipate static charge that may build up during operation of the printing machine.

The invention will now be described in more detail with reference the following examples.

## EXAMPLE 1

A coating formulation made in accordance with the present invention comprises 63.5% PTFE dispersion, 12.7% acrylic resin, 4.75% electrically conductive mica, 4.4% PFA dispersion, 4.04% triethanolamine, 1.09% butyl carbitol, and 1.09% of a 12% cerium octoate solution, and 1.1% nonionic surfactant (TRITON X-100, commercially available from Union Carbide Inc.). The balance of the formulation is water and additives. Each additive comprises less than 2% of the composition. The additives include well known defoamers, flow agents, dispersants, surfactants, stabilizers, thickeners, pigments, and/or fillers.

The exemplary coating described above is made as follows. 748 pounds of PTFE dispersion is added to 52 pounds of PFA dispersion and mixed for three minutes. The following solvents are mixed at high speed for 3-5 minutes and slowly added to the fluoropolymer dispersion mixture: 13 pounds of butyl carbitol, 15 pounds of Aromatic 150 (aromatic hydrocarbon mixture, CAS #64742-94-5), 47 pounds of triethanolamine, 13 pounds of Emersol 221 (oleic acid, CAS #112-80-1), 14 pounds of TRITON X-100, and 13 pounds of a 12% cerium octoate solution. 150 pounds of acrylic resin (NEOCRYL BT 44, commercially available from Zeneca Inc.) and 56 pounds of water are added and the mixture is mixed at low speed for 15 minutes. 56 pounds of electrically conductive mica are added and the mixture is put through a filter rated at 75 microns.

The wet non-stick coating formulation can be sprayed onto a substrate, such as a steel or aluminum fuser roller in a printing machine, by conventional or high volume, low pressure (HVLP) methods. The coating is preferably cured for 5 minutes at 820° F.

## EXAMPLE 2

A coating formulation made in accordance with the present invention comprises 61.7% polytetrafluoroethylene dispersion, 5.3% electrically conductive mica pigment, 3.8% triethylene glycol, 2.8% xylene, 2.0% propylene glycol, 0.2% silicone free defoamer, and 0.1% fluorosurfactant. The balance of the formulation is water and additives. Each additive comprises less than 2% of the composition. The additives include well known defoamers, flow agents, dispersants, surfactants, stabilizers, thickeners, pigments, and/or fillers.

The exemplary coating described above is made as follows. 221 pounds of water are mixed with 2 pounds of a silicone free defoamer. To this mixture is added a mixture of 44 pounds of triethylene glycol, 11 pounds of nonionic surfactant, 5 pounds of ethoxylated surfactant, and 0.5 pounds of a flow agent. The resultant mixture is mixed at high speed for three minutes. 33 pounds of xylene and 61 pounds of electrically conductive mica are added and mixed for 5 minutes. 24 pounds of blue pigment and 24 pounds of propylene glycol are ground together and added to the mixture. 718 pounds of a polytetrafluoroethylene dispersion, 7 pounds of white pigment, 0.5 pounds of flow agent and 2 pounds of surfactant are then added to the mixture. Thickener is added to adjust the viscosity. The formulation is filtered through a mesh filter rated at 75 microns.

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A preferred silicone free defoamer is commercially available from Troy Corporation under the trade name TROYKYD D999. A preferred ethoxylated surfactant is available from Air Products Corp. under the trade name SURFYNOL 440. A preferred fluorosurfactant is commercially available from 3M under the trade name FLUORAD FC129. A preferred dispersant is an acetylene diol dispersant that is commercially available from Air Products and Chemicals, Inc. under the trade name SURFYNOL 104BC. The remaining components are staple chemicals that are widely known and available.

The wet non-stick coating formulation can be sprayed onto a substrate, such as a steel or aluminum fuser roller in a printing machine, by conventional or high volume, low pressure (HVLP) methods. The coating is preferably cured for 5 minutes at 820° F.

While particular embodiments of the present invention have been illustrated and described above, the present invention should not be limited to such examples and descriptions. It should be apparent that changes and modifications may be incorporated and embodied as part of the present invention within the scope of the following claims.

The invention claimed is:

1. A roller for use in a printing machine, the roller comprising a first coating and second coating, the first coating including fluoropolymer and fibers of electrically conductive mica,

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the second coating being located above the first coating and including fluoropolymer and platelets of electrically conductive mica.

2. The roller of claim 1, wherein the color of the first and second coatings is not black.

3. The roller of claim 1, wherein the color of the roller is not black.

4. The roller of claim 1, wherein the first coating and the second coating do not include carbon black.

5. A method of dissipating static electricity in a printing machine roller, the method comprising the following steps:

- a. providing a printing machine roller;
- b. coating the printing machine roller with a first coating and second coating, the first coating including fluoropolymer and fibers of electrically conductive mica, the second coating being located above the first coating and including fluoropolymer and platelets of electrically conductive mica;
- c. curing the first and second coatings on the printing machine roller; and,
- d. installing the printing machine roller in a printing machine.

6. The method of claim 5, wherein the printing machine roller is a fuser roller.

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## **EXHIBIT B**



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(54) Title: COMPOSITION FOR USE AS NON-STICK COATING

(57) Abstract: A substrate with a non stick surface which is obtained by sequentially applying on the substrate and curing of at least three coating layers. All coating layers comprise a fluorocarbon resin and some other resins, the basecoat layer and the topcoat layer comprise inorganic particles.

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## COMPOSITION FOR USE AS NON-STICK COATING

### BACKGROUND OF THE INVENTION

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#### Field of the Invention

The present invention relates to compositions that can be used for non-stick coating applications.

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#### Prior Art

Non-stick coatings are well known in the art. In these coatings normally fluorocarbon resins are used, since these resins have a low surface energy as well as thermal and chemical resistance. However, non-stick coatings based upon fluorocarbon resins are limited with regard to abrasion resistance and resistance to flame contact, as well as adhesion to metal substrates. Such coatings are easily damaged when cut with a knife or another metal tool. Rubbing or sanding also easily wears these coatings away.

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Non-stick coatings may be applied in a single layer or as a multilayer coating.

One of the problems that is found when using non-stick coatings in frying pans is the absence of browning or searing of the products that are prepared in these pans. This has an impact on the appearance and taste of the products prepared in this way in comparison to products that are prepared in conventional cookware without a non stick coating.

The non-stick coatings according to the present invention combine the well known easy release properties of non-stick coatings with the searing of products.

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## SUMMARY OF THE INVENTION

According to the present invention such combination of properties can be obtained by sequential applying on a substrate and curing the following coating

5 compositions:

- a) A basecoat composition comprising
  - i. 5 – 15 wt.% of a fluorocarbon resin,
  - ii. 5 – 15 wt.% of an inorganic particle with an average particle size between 5 and 15 $\mu$ m, and
  - 10 iii. 20 – 30 wt% of a heat resistant binder resin,
- b) A midcoat composition comprising
  - i. 50 – 65 wt.% of a fluorocarbon resin,
  - ii. 5 – 15 wt.% of an acrylic resin, and
  - iii. 0 – 10 wt.% of a heat resistant binder resin,
  - 15 and
- c) A topcoat composition comprising
  - i. 50 – 65 wt.% of a fluorocarbon resin,
  - ii. 5 – 15 wt.% of an acrylic resin, and
  - iii. 3 – 10 wt.% of an inorganic particle with an average particle size between 15 and 20  $\mu$ m.
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Other embodiments of the invention comprise details concerning compositions, relative amounts of ingredients, particle sizes and method steps.

25 In this description wt.% refers to wt.% based on the total weight of a composition, unless specified otherwise.

## DETAILED DISCRIPTION OF THE INVENTION

### BASECOAT OR PRIMER COMPOSITION

In addition to the fluorocarbon resin, the inorganic particles, and heat resistant  
5 binder resin, the basecoat composition can comprise one or more of the  
following components: fillers, pigments surfactants, solvents, defoamers, and  
any other component for a coating composition known to the person skilled in  
the art.

In a preferred embodiment the basecoat composition is a waterborne  
10 composition, wherein all ingredients are dispersed in water or are water-  
soluble.

### MIDCOAT COMPOSITION

In addition to the fluorocarbon resin, the acrylic resin, and heat resistant binder  
15 resin, the midcoat composition can comprise one or more of the following  
components: fillers, pigments surfactants, solvents, defoamers, and any other  
component for a coating composition known to the person skilled in the art.

In a preferred embodiment the midcoat composition is a waterborne  
composition, wherein all ingredients are dispersed in water or are water-  
20 soluble.

### TOPCOAT COMPOSITION

In addition to the fluorocarbon resin, the acrylic resin, and the inorganic  
particles, the topcoat composition can comprise one or more of the following  
25 components: fillers, pigments surfactants, solvents, defoamers, and any other  
component for a coating composition known to the person skilled in the art.

In a preferred embodiment the topcoat composition is a waterborne  
composition, wherein all ingredients are dispersed in water or are water-  
soluble.

#### FLUOROCARBON RESIN

Examples of fluorocarbon resins that can be used in the present invention include polytetrafluoroethylene (PTFE), and copolymers of tetrafluoroethylene (TFE) with hexafluoropropylene (HFP), perfluoropropylvinyl ether (PPVE),  
5 perfluoroalkyl vinyl ether, and ethylene. Commercial examples are tetrafluoroethylene-hexafluoropropylene copolymers (FEP), tetrafluoroethylene-perfluoroalkyl vinyl ether copolymers (PFA), ethylene-tetrafluoroethylene copolymers (ETFE). Also mixtures of any of the above polymers, copolymers and monomers can be used.

10

If the contemplated application or use of the coated item is high temperature, the selection of fluoropolymer(s) should be those that are heat stable.

PTFE is an example of a heat resistant or stable fluorocarbon resins that can  
15 be used according to the present invention.

Fluorocarbon resins that are melt flowable at a temperature above 300°C include copolymers of TFE, e.g., FEP and PFA.

20 The fluorocarbon resins are generally available as a dispersion of the polymer in water. In this dispersion the polymer particles have a small size (usually around 0,2  $\mu\text{m}$ ) and a surfactant is used to obtain a stable dispersion. For some polymers it is desirable to include an organic liquid in the dispersion.

25 The fluorocarbon resin can also be present as a polymer powder, in which case normally an organic liquid is used to mix the particles into the coating composition.

#### HEAT RESISTANT BINDER RESIN (ADHESION PROMOTER)



The heat resistant binder resin that is present in the primer or basecoat composition and that can be present in the midcoat composition is a polymer that is film-forming upon heating (such as by radiation), evaporation of the solvent, and is also thermally stable. The binder shows good adhesion to the substrate and to the fluoropolymer composition that is applied over the primer or midcoat composition. Preferred binders are those that are soluble or solubilized in water or a mixture of water and one or more organic solvents for the binder. This solvent should be miscible with water. The solubility of the binder enhances the mixing of the binder with the other components that are present in the primer composition. An example of a suitable heat resistant binder component is a polyamic acid resin (PAI), which converts to a polyamideimide upon heating. This binder when fully imidized is able to withstand a continuous service temperature in excess of 250°C. In general, the polyamic acid is dissolved in a suitable combination of a solvent, such as N-methylpyrrolidone, water, and suitable tertiary alkyl amine. Another example of a suitable heat resistant binder component is polyethersulfone (PES). These polymers can withstand a continuous service temperature in the range from 170°C to 190°C. Also polyphenylene sulphide (PPS) can be used as a heat resistant binder, either alone or in a mixture with PAI or PES.

Examples of heat resistant binders that can be used according to the present invention include Torlon® AI-10 (ex. Solvay), and Radel A-300 (ex. Solvay).

#### ACRYLIC RESIN

The midcoat composition and the topcoat composition comprise an acrylic resin. In principle any acrylic resin can be used in these coating compositions. In a preferred embodiment the acrylic resin has a  $T_g$  in the range of 40 – 70°C. In a further preferred embodiment, the acrylic resin is a water-dispersable acrylic resin.

#### INORGANIC INERT PARTICLES

The basecoat composition and the topcoat composition comprise inorganic particles, which are inert with respect to the other components that are present in the composition and can withstand a continuous service temperature in excess of 250°C. In addition, these particles are also stable at the eventual  
5 baking temperature of the non-stick coating. The particles are also not soluble in water or any other solvent that is present in the primer composition. Examples of suitable inorganic particles include inorganic oxides, carbides or nitrides of elements in groups IIA – VB of the periodic table and natural minerals. In the basecoat the inorganic particles have an average particle size  
10 in the range from about 5 to about 15 µm, in the topcoat the inorganic particles have an average particle size in the range from about 15 to about 20 µm. The inorganic particles have a preferred Mohs hardness of at least about 5, more preferably a mohs hardness of at least about 6. Examples of inorganic particles with Mohs hardness above 5 include alumina, zirconia, silicon carbide, titanium  
15 carbide, aluminium boride, and cristobalite.

In addition to the inorganic inert particles mentioned above, the coating compositions used according to the present invention can also comprise fillers, additives, and pigments that are commonly used in the preparation of coating  
20 compositions. Fillers can be any fillers known to those skilled in the art, e.g., barium sulfate, calcium sulfate, calcium carbonate, silicas or silicates (such as talc, feldspar, and china clay). Additives such as stabilizers, antioxidants, leveling agents, antissettling agents, matting agents, rheology modifiers, surface-active agents, UV light absorbers, light stabilizers, amine synergists,  
25 waxes, or adhesion promoters can also be added.

#### APPLICATION OF THE COATING

The substrates coated according to the present invention can be aluminium shaped articles, such as pots, pans, lids, mixing spoons, and all other utensils  
30 usually employed for food preparation and cooking (baking pans, oven racks etc.) as well as aluminium sheet to be shaped into the aforesaid articles. In

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both cases, the aluminium support is simply degreased according to any known method, e.g., in an alkaline or acid environment, or with organic solvents. In this treatment, the aluminium support maintains the surface roughness of the aluminium sheet, i.e. below 1,2  $\mu\text{m}$ . In addition to the degreasing it is possible  
5 to roughen the surface, e.g. by sand blasting or grinding, before application of the primer. However, this is not necessary.

In a next step the basecoat composition is applied and the coated article is dried until the coating is touch dry. This drying can be done in an oven. In a  
10 further step the midcoat composition and the topcoat composition are applied. In one embodiment, the midcoat is dried before the topcoat is applied. In another embodiment, the midcoat composition and the topcoat composition are applied wet-on-wet.

15 Finally, the substrate is baked in an oven at a temperature between 380°C and 440°C, preferably between 410°C and 430°C.

The invention will be elucidated with reference to the following examples. These are intended to illustrate the invention but are not to be construed as  
20 limiting in any manner the scope thereof.

### Examples

The following applies to the examples given below:

25

#### Scotch Brite abrasion test

The Scotch Brite Abrasion' Test measures a coating's resistance to a constant scrubbing with an abrasive scouring pad. The vertical load on the scouring pad  
30 is set to 10 pounds (4.54 kg), and the scouring pad is changed every 10,000 strokes. The number of cycles that are required to scrape the coating down to

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bare metal is recorded in order to gauge the abrasion resistance of the non-stick system.

#### Egg Release test

5

A pan coated with non-stick coating is heated to 150 ° C, after which an egg is fried. The level of release is rated as follows;

##### Egg release grading scale (cleaning with dishwasher detergent/water)

1. Very poor: Egg sticks to wear track and difficult to clean
- 10 2. Very poor: Egg sticks to wear track but cleaning somewhat easier
3. Very poor: Egg sticks to 90% of wear track but cleaned fairly easy
4. Very poor: Egg sticks to 80% of wear track but cleaned fairly easy
5. Poor: Egg sticks to 70% of wear track but cleaned fairly easy
6. Fair: Egg sticks to 60% of wear track but cleaned fairly easy
- 15 7. Fair: Egg sticks to 20-40% of wear track but cleaned fairly easy
8. Good: Egg sticks to 10% of wear track but cleaned easily
9. Very good: Egg could be removed intact with some difficulty, easy cleaning
10. Excellent: Clean removal of egg intact, no residue left.

#### 20 Hand Held Tiger Paw test

The hand held "Tiger Paw" device is an industry-accepted standard, which was designed to test the resistance of a non-stick coating to long-term kitchen abuse. The Hand Held Tiger Paw consists of a weighted apparatus, which uses  
25 three "ball point" pens to scratch the coating film. The cookware which is being tested is filled with a thin layer of cooking oil, and heated to 400° Fahrenheit (205° Celsius.)



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The Tiger Paw is rotated over the non-stick surface in a circular fashion 2000 times, changing direction every 100 rotations. The coating is then examined for any fraying, blistering, or penetration to bare metal.

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## 1. Comparative example 1

	Basecoat		Middle coat		Topcoat	
	Raw material	Wt%	Raw material	Wt%	Raw material	Wt%
1	Deionized water	61.3	Black pigment	0.2	Hydrocarbon Solvent	1.4
2	N-methylpyrrolidone	3.4	Hydrocarbon Solvent	1.3	Titania coated mica, EM Ind	0.3
3	Furfuryl Alcohol	2.4	Titania coated mica, EM Ind	0.5	Cerium octoate	1.2
4	Triton X100 surfactant	3.0	Cerium octoate	1.2	PTFE emulsion	62.3
5	Aluminum Oxide	0.8	PTFE emulsion	60.1	FEP emulsion	2.2
6	PTFE emulsion	16.0	FEP emulsion	2.1	Deionized water	14.9
7	Black pigment	0.6	Deionized water	17.9	Triethanolamine	4.3
8	Ultramarine blue pigment	5.0	Triethanolamine	4.0	Oleic Acid	1.1
9	FEP emulsion	1.0	Oleic Acid	1.2	Acrylic emulsion	12.0
10	Polyamide-imide	6.5	Acrylic emulsion	11.5	Aluminum Oxide	0.3
		100.0		100.0		100.0

## 5 1. Comparative example 2

	Basecoat		Middle coat		Topcoat	
	Raw material	Wt %	Raw material	Wt%	Raw material	Wt%
1	Deionized water	52.8	Black pigment	0.2	Hydrocarbon Solvent	1.4
2	N-methylpyrrolidone	3.4	Hydrocarbon Solvent	1.3	Titania coated mica, EM Ind	0.3
3	Furfuryl Alcohol	2.4	Titania coated mica, EM Ind	0.5	Cerium octoate	1.2
4	Triton .RTM. X100 surfactant	3.0	Cerium octoate	1.2	PTFE emulsion	62.3
5	Aluminum Oxide	0.6	PTFE emulsion	60.1	FEP emulsion	2.2
6	PTFE emulsion	16.0	FEP emulsion	2.1	Deionized water	14.9
7	Black pigment	0.3	Deionized water	17.9	Triethanolamine	4.3
8	Ultramarine blue pigment	5.0	Triethanolamine	4.0	Oleic Acid	1.1
9	FEP emulsion	1.0	Oleic Acid	1.2	Acrylic emulsion	12.0
10	Polyamide-imide	6.5	Acrylic emulsion	11.5	Aluminum Oxide	0.3
11	Silicon carbide	9.0				
		100		100.		100.

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## 2. Example (sear coating)

Basecoat			Middle coat		Topcoat	
	Raw material	Wt%	Raw material	Wt%	Raw material	Wt%
1	Deionized water	49.5	Hydrocarbon Solvent	1.2	Hydrocarbon Solvent	0.9
2	N-methylpyrrolidone	2.4	Titania coated mica, EM Ind	4.9	Titania coated mica, EM Ind	0.8
3	Furfuryl Alcohol	1.2	Cerium octoate	0.9	Cerium octoate	0.9
4	Triton .RTM. X100 surfactant	0.95	PTFE emulsion	55.0	PTFE emulsion	53.5
5	Aluminum Oxide	5.0	FEP emulsion	3.9	FEP emulsion	3.7
6	PTFE emulsion	8.3	Deionized water	15.7	Deionized water	19.6
7	Black pigment	0.25	Triethanolamine	3.5	Triethanolamine	3.4
8	Ultramarine blue pigment	4.0	Oleic Acid	1.2	Oleic Acid	0.9
9	FEP emulsion	0.88	Acrylic emulsion	11.5	Acrylic emulsion	10.7
10	Polyamide-imide	6.5	Polyethersulfone	1.2	Silicon carbide	5.4
11	Silicon carbide	11.0			Black pigment	0.2
		100.0		100.0		100.0

- 5 In these examples, the consecutive coating layers were sprayed on a grit blast frying pan at a total film thickness of around 25-32 microns. After a flash bake for 3-5 minutes at 80-120°C, then final cure was done for 3-5 minutes at 427-432°C. Performance comparison of these examples was listed as below.

		Comparative example 1	Comparative example 2	Example (sear coating)
1	Egg release	8	9	9
2	Tiger paw	500 cycles	900 cycles	2,600 cycles
3	AIHAT	3 cycles	7 cycles	21 cycles
4	Abrasion	10,000cycles	90,000cycles	150,000cycles

10

From the above test result, it is clearly shown that the substrate with the coating in accordance to the present invention shows excellent performance.



## Claims

1. A substrate with a non stick surface, said non stick surface obtained by sequential applying on the substrate and curing the following coating compositions:
  - a) A basecoat composition comprising
    - iv. 5 – 15 wt.% of a fluorocarbon resin,
    - v. 5 – 15 wt.% of an inorganic particle with an average particle size between 5 and 15 $\mu$ m, and
    - vi. 20 – 30 wt% of a heat resistant binder resin,
  - b) A midcoat composition comprising
    - vii. 50 – 65 wt.% of a fluorocarbon resin,
    - viii. 5 – 15 wt.% of an acrylic resin, and
    - ix. 5 – 10 wt.% of a heat resistant binder resin,and
  - c) A topcoat composition comprising
    - x. 50 – 65 wt.% of a fluorocarbon resin,
    - xi. 5 – 15 wt.% of an acrylic resin, and
    - xii. 3 – 10 wt.% of an inorganic particle with an average particle size between 15 and 20  $\mu$ m.
2. A substrate according to claim 1, characterised in that the basecoat and the topcoat comprise inorganic particles selected from the group consisting of alumina, zirconia, silicon carbide, titanium carbide, aluminum boride, and cristobalite.
3. A process for the preparation of the substrate according to claim 1 wherein in a first step the basecoat is applied to the substrate and dried, in a next step the midcoat is applied on top of the basecoat and dried, and in a further step the topcoat is applied on top of the midcoat,

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and in a final step the thus obtained coated substrate is baked at a temperature between 380°C and 440°C.

4. A process according to claim 1 wherein the acrylic resin has a  $T_g$  in the range of 40 – 70°C.
- 5

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/CN2009/070381

**A. CLASSIFICATION OF SUBJECT MATTER**

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC: A61K, A61P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EPODOC, PAJ, CA, MEDLINE, EMBASE: FLUOROCARBON, ACRYLIC, NON-STICK, NON STICK, +FLUOROCARBON, ACRYL+, RESIN, INORGANIC, PARTICLE, GRAIN, GRANULE

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN101330986A(MITSUI DU PONT FLUORO-CHEMICAL), 24 Dec. 2008(24.12.2008) See claims 1-20, examples 1-3	1-4
X	CN1315984A(DU PONT DE NEMOURS & CO E I), 03 Oct. 2001(03.10.2001) See claims 1-16, page 8 lines 23-32, page 9 lines 1-12, page 10 lines 13-19, tables 1-3	1-4

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
28 Oct.2009(28.10.2009)Date of mailing of the international search report  
**26 Nov. 2009 (26.11.2009)**Name and mailing address of the ISA/CN  
The State Intellectual Property Office, the P.R.China  
6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China  
100088  
Facsimile No. 86-10-62019451

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2009/070381

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.

PCT/CN2009/070381

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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.

PCT/CN2009/070381

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**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/CN2009/070381

**CLASSIFICATION OF SUBJECT MATTER**

B05D5/08 (2006.01) i

A47J36/02 (2006.01) i

A47J37/10 (2006.01) i

A47J27/00 (2006.01) i

C09D127/12 (2006.01) i

C09D127/14 (2006.01) i

C09D127/18 (2006.01) i

## **EXHIBIT C**



June 2, 2008

Nanochem Technologies, Ltd.  
4715 Pine Creek Road  
Elkhart, IN 46516

Gentlemen:

Akzo Nobel Non-Stick Coatings LLC (hereafter to as "Akzo Nobel") and Nanochem Technologies, Ltd. (hereafter referred to as "Nanochem"), in accordance with this Agreement of the above date, wish to exchange information for the purpose of determining whether Nanochem might toll manufacture certain products for Akzo Nobel (Purpose). Akzo Nobel will disclose formulas, product specifications, sales forecasts and processing know-how. Nanochem may disclose their processing know-how. The information provided by both parties hereunder is collectively referred to as "Confidential Information". Akzo Nobel may also provide samples of product and color standards to Nanochem (Samples) for the in furtherance of the Purpose. Samples are considered Confidential Information, including the results of any investigations of said Samples.

The parties are to exchange Confidential Information and Akzo Nobel is to provide Samples, only for carrying out the above purpose.

The foregoing restrictions on disclosure and use shall not be applicable to any Confidential Information that the receiving party can demonstrate:

(i) to have been rightfully in its possession prior to the date of this Agreement;

(ii) to have been in the public domain prior to the date of this Agreement;

(iii) to have become a part of the public domain by publication or other means, except an unauthorized act or omission by the receiving party; or

(iv) to have been supplied to the receiving party by a third party as a matter of right without restriction on use or disclosure; or

Confidential Information shall not be considered within the above exceptions merely because the Confidential Information is embraced by more general information within the exception. Any combination of features of Confidential Information shall not be considered within the above exceptions merely because individual features, as opposed to the combination itself and its principles of operation, are within the exceptions.

Nanochem agrees to not analyze, determine or attempt to determine the chemical composition and/or physical structure of Samples, except to the extent necessary to carry out the Purpose, unless written authorization to the contrary is provided by Akzo Nobel. Nanochem further agrees to not make available any portion of Samples to any third party and shall prevent access by any third party to any portion of Samples, unless permitted otherwise by Akzo Nobel.

A receiving party shall limit access to Samples (in the case of Nanochem) and Confidential Information of the disclosing party to only those of its employees who need access in order to effectuate this Agreement, and to the extent such employees are not already so obligated by employment

agreement or otherwise, the parties shall require by express written agreement that such employees maintain said Confidential Information in confidence and that they shall use such information and Samples only in accordance with the terms of this Agreement.

Upon the written request of Akzo Nobel, Nanochem shall return any and all quantities of the Samples provided then in the Nanochem's possession. There are no express or implied warranties on Samples, and each Akzo Nobel expressly disclaims the implied warranties of merchantability and fitness for a particular use. The Samples may be experimental, and Nanochem shall handle in accordance with instructions.

Neither Party will make any public statements with respect to the business, personnel, or affairs, including the existence of this Agreement, nor use the name, trademark, or likeness of the other Party, without express prior written consent of an authorized representative of such Party.

At any time upon the written request of the disclosing party, the recipient party shall, within a reasonable time, destroy and confirm destruction to the disclosing party, all written or physical embodiments, including all copies, of the disclosing party's Confidential Information disclosed to the recipient party and then in its possession; provided, however, that each party may retain one copy of Confidential Information for archival purposes.

Neither this agreement, the providing of Samples, nor the disclosure of Confidential Information hereunder by either party shall be deemed by implication or otherwise to vest in the other party any present or future rights in any patents, trade secrets or intellectual property of the providing or disclosing party and no license is granted except as explicitly stated herein. The obligations of confidentiality of a recipient hereunder specifically prohibit filing any applications for patent or other protection that disclose Confidential Information of the disclosing party.

The nondisclosure and nonuse provisions under this agreement shall remain in effect for a period of ten (10) years from the date of this agreement.

This Agreement shall not be assignable by either party without the prior written consent of the other party, except to a successor of the entire business pertinent to the field of this Agreement of the assigning party, subject to the approval of the other party, which approval shall not be unreasonably withheld. No assignment shall be valid until the assignee has assumed the rights and obligations of the assigning party under this Agreement. Any assignment of this Agreement shall not relieve the assignor of the restrictions on use, duplication and disclosure of Confidential Information as set forth herein.

Each party acknowledges that any breach of this Agreement will cause irreparable harm to the other party and that money damages will not provide an adequate remedy therefore. Each party, therefore, agrees and consents to the granting of injunctive or other equitable relief in favor of the other party, without requirement of a bond, as a remedy for any such breach, in addition to all other remedies now or hereafter existing at law, in equity, by statute or otherwise.

If either party is required by law, including without limitation pursuant to the terms of a subpoena or other similar document, to disclose Confidential Information of the other party, said first party shall immediately advise the other party to allow the other party to seek a protective order. Absent any such protective order, the receiving party shall be permitted to disclose only such Confidential Information as it is advised by counsel must be disclosed by law.

Each receiving party agrees to fully comply with the U.S. Export Administration Laws and Rules to the extent such Rules apply to Confidential Information received hereunder, and further agrees to not export, re-export or otherwise transfer any such Confidential Information to any prohibited country

as defined by the U.S. Export Administration Regulations unless properly authorized by the U.S. Government and prior written permission is received from the other party.

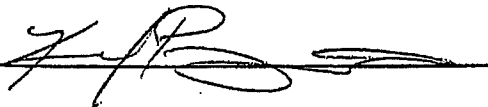
This Agreement shall be interpreted according to the laws of the State of Illinois without giving effect to its conflict of law provisions. The Agreement shall come into force on the effective date stated at the top of page 1 and shall terminate two (2) years thereafter. The obligations of confidentiality and non-use shall survive termination as agreed herein.

The Parties shall attempt in good faith to resolve promptly any dispute arising out of, or in connection with, this Agreement by negotiation. If such dispute has not been resolved by negotiation within twenty (20) days of the disputing party's written notice, or if the Parties fail to meet within twenty (20) days as from such notice, the Parties shall endeavor to settle the dispute by mediation under the supervision of and in accordance with the CPR Model Mediation Procedure for Business Dispute. Unless otherwise agreed, both Parties or each individual party may request the CPR to appoint an independent mediator. The language of mediation shall be English and the seat of mediation shall be agreed upon by both Parties, and, in the event the Parties do not timely agree, the seat will be determined by the mediator. If the dispute has not been resolved by non-binding means as described herein within forty five (45) days of the initiation of such procedure, the dispute shall be finally and exclusively settled by the courts of the State of Illinois. No negotiation or mediation shall be deemed to vitiate or reduce the obligations and liabilities of the parties or deemed a waiver by a party of any claims or remedies to which the party would otherwise be entitled. Any and all statements made in the course of such negotiation or mediation shall be strictly off the record and shall not be admissible in any court or arbitration proceeding. This paragraph shall not be construed to limit or to preclude either party from bringing any legal action for injunctive or other provisional relief as necessary or appropriate.

The parties indicate their agreement to the foregoing terms and conditions by having both counterparts of this Agreement executed by a duly authorized representative and each retaining one fully executed counterpart.

Yours truly,

AKZO NOBEL NON-STICK COATINGS LLC

By: 

Title: SALES MANAGER

Date: 6/4/08

By: Dan Detzler

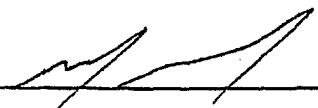
Title: Operations Manager

Date: 6-4-08

We hereby confirm our agreement on the foregoing:



NANOCHEM TECHNOLOGIES, LTD.

By:  \_\_\_\_\_

Title: VP Sales \_\_\_\_\_

Date: 6/6/08 \_\_\_\_\_

## **EXHIBIT D**

LAW OFFICES  
**WEIR & PARTNERS LLP**  
THE WIDENER BUILDING • SUITE 500  
1339 CHESTNUT STREET  
PHILADELPHIA, PA 19107

(215) 665-8181  
(215) 665-8464 FAX

Walter Weir, Jr.  
Member of PA, NJ Bar

Direct Dial (215) 241-7751  
E-mail: [wweir@weirpartners.com](mailto:wweir@weirpartners.com)

March 10, 2010

*Via Overnight Mail Delivery*

Nanochem Technologies, Ltd.  
1179 Kent Street  
Elkhart, Indiana 46514-1741

Attention: Mr. Jeffrey W. Schwartz, President  
Mr. Richard J. Lutz, Vice President/General Manager

Dear Messrs. Schwartz and Lutz:

This firm is legal counsel to Whitford Worldwide Company, and its subsidiary and affiliated entities (collectively, "Whitford"), whose principal place of business in the United States is located at 47 Park Avenue, Elverson, Pennsylvania. Whitford is engaged in the business of developing and manufacturing a wide variety of non-stick coatings used in many consumer and commercial applications ranging from cookware, bakeware and appliances to textiles, fasteners, automobiles and coatings for chemical processing industries and the petrochemical industry.

In May 2009, Whitford completed a transaction with Akzo Nobel Coatings International B.V. and its affiliates (collectively, "Akzo Nobel") pursuant to which Whitford acquired all of the liquid non-stick coating business, and the powder non-stick coating business for cookware and bakeware, of Akzo Nobel throughout the world, including without limitation, at Akzo Nobel's locations in the United States.

Whitford is aware that Akzo Nobel and Nanochem Technologies, Ltd. ("Nanochem") entered into a Non-Disclosure Agreement dated June 2, 2008 ("Agreement") relating to the possession and use by Nanochem of certain confidential information belonging to Akzo Nobel including without limitation, "...formulas, product specifications, sales forecasts and processing know-how." A copy of this Agreement is enclosed with this letter for your reference. Akzo Nobel's confidential information described in the Agreement, as well as the benefits of the provisions imposing restrictions on Nanochem's disclosure and use of this confidential information, were acquired by Whitford as part of its transaction with Akzo Nobel.

WEIR & PARTNERS LLP

Nanochem Technologies, Ltd.

Page 2

Whitford has good reason to believe that Nanochem is in breach of the terms and conditions of the Agreement in that Nanochem is using confidential information in its possession, which previously belonged to Akzo Nobel and is now owned by Whitford, to manufacture and sell non-stick coating products to third parties. These actions by Nanochem constitute a clear violation of the Agreement which remains in full force and effect.

It should come as no surprise to you that because of its substantial investment in the non-stick coating business purchased from Akzo Nobel, Whitford intends to vigorously enforce its rights and remedies in situations such as that presented by Nanochem's breach of the Agreement. To that end, if necessary, Whitford is prepared to take appropriate legal action against Nanochem to protect its proprietary interest in the confidential information acquired from Akzo Nobel which is the subject of the Agreement.

On behalf of our client, therefore, demand is made that Nanochem IMMEDIATELY CEASE AND DESIST from utilizing any confidential information previously belonging to Akzo Nobel and now owned by Whitford in violation of the restrictions on disclosure and use of this confidential information, as set forth in the Agreement.

Nanochem has five (5) calendar days from the date of this letter to contact us and confirm, by providing us with such written information and/or documentation as we deem satisfactory, of Nanochem's compliance to these demands. If Nanochem fails to comply with these demands, Whitford will have no choice but to proceed in a manner appropriate to protect its rights. Nanochem's failure to comply with these demands may expose Nanochem to an action for injunctive relief or other monetary damages and any other relief permitted under state and federal law, including court costs, attorneys' fees and punitive damages.

Please be so advised.

Very truly yours,

Walter Weir, Jr.

WWJR/kmm

cc: David P. Willis, Jr., President, Whitford Worldwide Company  
Brian Kilty, Chief Financial Officer, Whitford Worldwide Company

LAW OFFICES  
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A Pennsylvania Limited Liability Partnership

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Member Pennsylvania and  
New Jersey Bar

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E-Mail: [sgiroux@weirpartners.com](mailto:sgiroux@weirpartners.com)

April 15, 2010

VIA ELECTRONIC MAIL ([james.brotherson@bakerd.com](mailto:james.brotherson@bakerd.com))

James R. Brotherson, Esquire  
Baker & Daniels LLP  
202 South Michigan Street  
Suite 1400  
South Bend, IN 46601

Re: Nanochem Technologies, LLC/Whitford Worldwide Company

Dear Mr. Brotherson:

I am writing this letter with further reference to the March 16, 2010 letter to you from Walter Weir, Jr. of this firm.

As you may recall, Mr. Weir sent a letter to Nanochem Technologies, LLC ("Nanochem") dated March 10, 2010 in which he indicated that our client, Whitford Worldwide Company ("Whitford"), has good reason to believe that Nanochem is in breach of the July 2, 2008 Non-Disclosure Agreement between Nanochem and Akzo Nobel Non-Stick Coatings LLC ("Akzo Nobel") in that Nanochem is using confidential information in its possession, which previously belonged to Akzo Nobel and is now owned by Whitford, to manufacture and sell non-stick coating products to third parties.

You responded to Mr. Weir by letter dated March 12, 2010 which stated in part "... Nanochem does not use any formulations or Akzo Nobel samples in furtherance of Nanochem's business." In his March 16<sup>th</sup> letter, Mr. Weir requested that you provide us with information in the nature of an audit trail reflecting the fact that all samples and formulas from Akzo Nobel were returned by Nanochem. Despite the fact that nearly one month has passed, we still have not received the information from you requested by Mr. Weir in his letter of March 16<sup>th</sup>.

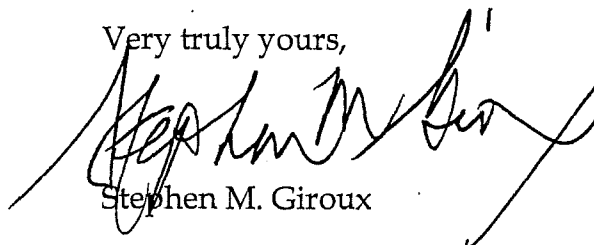
WEIR & PARTNERS LLP

James R. Brotherson, Esquire  
Baker & Daniels  
Page 2

Whitford continues to have serious concerns that Nanochem has misappropriated formulas, samples and other confidential information rightfully belonging to Whitford in violation of the Non-Disclosure Agreement between Nanochem and Akzo Nobel. Therefore, we are repeating our request for supporting information confirming the representation made in your March 12<sup>th</sup> letter to Mr. Weir, and we are requesting that such information be provided within five (5) calendar days from the date of this letter. Otherwise, Whitford will have no alternative but to pursue appropriate action to protect its rights with respect to such confidential information.

Finally, I want to make you aware of the fact that Whitford has engaged the services of Adam F. Cox, Esquire of your firm to represent Whitford for the past several years in connection with virtually all aspects of Whitford's United States patent work. In fact, I have personally worked with Mr. Cox on Whitford-related matters. It would appear, therefore, to be a conflict of interest for your firm to represent Nanochem with respect to this potential dispute. However, it is our hope that this matter can be quickly resolved in an amicable fashion upon receipt of the requested information so that any controversy between Nanochem and Whitford can be avoided.

Very truly yours,



Stephen M. Giroux

SMG/kmm

cc: Mr. David P. Willis, Jr.  
Mr. Brian Kilty



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New Jersey Bar

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E-Mail: [sgiroux@weirpartners.com](mailto:sgiroux@weirpartners.com)

May 7, 2010

**VIA ELECTRONIC AND REGULAR MAIL**  
([james.brotherson@bakerd.com](mailto:james.brotherson@bakerd.com))

James R. Brotherson, Esquire  
Baker & Daniels LLP  
202 South Michigan Street  
Suite 1400  
South Bend, IN 46601

Re: Nanochem Technologies, LLC/Whitford Worldwide Company

Dear Mr. Brotherson:

I am writing with further reference to my April 15, 2010 letter to you, a copy of which is enclosed for your convenience.

As you are aware, the potential conflict of interest in connection with your firm's representation of Nanochem Technologies, LLC ("Nanochem") has been resolved with our client, Whitford Worldwide Company ("Whitford"), by letter dated April 20, 2010, consenting to your representation of Nanochem and agreeing to waive any potential conflict of interest, provided that Baker & Daniels LLP may not represent Nanochem in any litigation adverse to Whitford that may arise with respect to this matter.

To date, I have received no response from you to my April 15<sup>th</sup> letter, nor have I even received the courtesy of an acknowledgment of this correspondence and an indication of whether or not you intend to reply. My client and I find this lack of communication from you not only troubling, but also most puzzling under these somewhat unusual circumstances.

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James R. Brotherson, Esquire  
Baker & Daniels  
Page 2

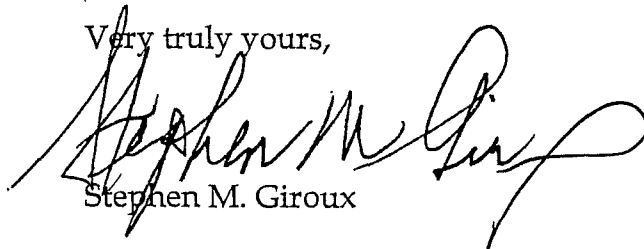
Please advise me as soon as possible by whatever means you think appropriate whether or not you intend to reply to my April 15<sup>th</sup> letter, and if so, when I can expect to receive a meaningful and responsive reply. If your firm is no longer representing Nanochem in this matter, please so indicate and provide me with the contact information for Nanochem's new legal counsel.

As I hope is abundantly clear to you by now, Whitford strongly believes that Nanochem has misappropriated formulas, samples and other confidential information rightfully belonging to Whitford in violation of the July 2, 2008 Non-Disclosure Agreement between Nanochem and Akzo Nobel Non-Stick Coatings, LLC ("Akzo Nobel") and has no intention of letting this matter drop. Accordingly, if we do not receive a substantive response to my April 15<sup>th</sup> letter by the close of business on Wednesday, May 12, 2010, Whitford will, without further notice to you or your client, take appropriate action to protect its interests with respect to the misappropriation of the confidential information by Nanochem. In the event that litigation is initiated by Whitford, which is certainly a strong possibility at the moment, your firm will not be permitted to represent Nanochem.

It remains Whitford's preference to discuss and resolve this matter without the necessity of litigation. However, your failure to provide us with a constructive and meaningful response, and to furnish the documentation we have repeatedly requested to support your contention that Nanochem does not use formulas previously belonging to Akzo Nobel and now owned by Whitford in furtherance of its business, and to confirm that all samples and formulas from Akzo Nobel have been returned by Nanochem, will leave my client no alternative but to commence such action to protect its interests.

Please be guided accordingly.

Very truly yours,



Stephen M. Giroux

SMG/kmm

cc: Mr. David P. Willis, Jr.  
Mr. Brian Kilty

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Edward T. Kang  
Member of PA, NJ and NY Bars

Direct Dial (215) 241-7764  
E-Mail: ekang@weirpartners.com

June 10, 2010

**VIA ELECTRONIC MAIL** ([james.brotherson@bakerd.com](mailto:james.brotherson@bakerd.com))  
**& FIRST CLASS MAIL**

James R. Brotherson, Esquire  
Baker & Daniels LLP  
202 South Michigan Street  
Suite 1400  
South Bend, IN 46601

**Re: Nanochem Technologies, LLC/Whitford Worldwide Company**

Dear Mr. Brotherson:

I am litigation counsel on behalf of Whitford Worldwide Company. Whitford believes your client Nanochem Technologies, LLC is in breach of the July 2, 2008 Non-Disclosure Agreement entered between it and Akzo Nobel Non-Stick Coatings LLC, which agreement has been assigned to Whitford, by its using confidential formulas and samples covered under the agreement.

We asked you, on at least three occasions, to provide us with information substantiating your claim that "Nanochem does not use any formulations or Akzo Nobel samples in furtherance of Nanochem's business." The last correspondence we sent you was on May 7, 2010, and, yet, we have not heard from you.

You should consider this letter our last request that you provide us with information supporting your claim, including all materials showing that all confidential samples and formulas have been

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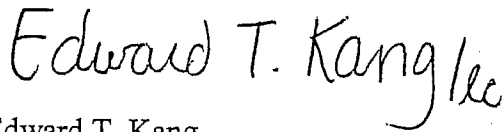
James R. Brotherson, Esquire

June 10, 2010

Page 2 of 2

returned by Nanochem. Without receiving your timely response, I will have no choice but to conclude that Nanochem is breaching its obligations to Whitford and take appropriate actions.

Very truly yours,

Handwritten signature of Edward T. Kang in cursive script.

Edward T. Kang

ETK/lmc

cc: Mr. David P. Willis, Jr. (via facsimile)  
Mr. Brian Kilty (via facsimile)  
Mr. Michael Miller (via facsimile)